Polarization of nuclear spins by a cold nanoscale resonator

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A cold nanoscale resonator coupled to a system of nuclear spins can induce spin relaxation. In the low-temperature limit where spin-lattice interactions are "frozen out," spontaneous emission by nuclear spins into a resonant mechanical mode can become the dominant mechanism for cooling the spins to thermal equilibrium with their environment. We provide a theoretical framework for the study of resonator-induced cooling of nuclear spins in this low-temperature regime. Relaxation equations are derived from first principles, in the limit where energy donated by the spins to the resonator is quickly dissipated into the cold bath that damps it. A physical interpretation of the processes contributing to spin polarization is given. For a system of spins that have identical couplings to the resonator, the interaction Hamiltonian conserves spin angular momentum, and the resonator cannot relax the spins to thermal equilibrium unless this symmetry is broken by the spin Hamiltonian. The mechanism by which such a spin system becomes "trapped" away from thermal equilibrium can be visualized using a semiclassical model, which shows how an indirect spin-spin interaction arises from the coupling of multiple spins to one resonator. The internal spin Hamiltonian can affect the polarization process in two ways: (1) By modifying the structure of the spin-spin correlations in the energy eigenstates, and (2) by splitting the degeneracy within a manifold of energy eigenstates, so that zero-frequency off-diagonal terms in the density matrix are converted to oscillating coherences. Shifting the frequencies of these coherences sufficiently far from zero suppresses the development of resonator-induced correlations within the manifold during polarization from a totally disordered state. Modification of the spin-spin correlations by means of either mechanism affects the strength of the fluctuating spin dipole that drives the resonator. In the case where product states can be chosen as energy eigenstates, spontaneous emission from eigenstate populations into the resonant mode can be interpreted as independent emission by individual spins, and the spins relax exponentially to thermal equilibrium if the development of resonator-induced correlations is suppressed. When the spin Hamiltonian includes a significant contribution from the homonuclear dipolar coupling, the energy eigenstates entail a correlation specific to the coupling network. Simulations of dipole-dipole coupled systems of up to five spins suggest that these systems contain weakly emitting eigenstates that can trap a fraction of the population for time periods $\gg 100/R_0$, where R_0 is the rate constant for resonator-enhanced spontaneous emission by a single spin 1/2. Much of the polarization, however, relaxes with rates comparable to R_0. A distribution of characteristic high-field chemical shifts tends to increase the relaxation rates of weakly emitting states, enabling transitions to states that can quickly relax to thermal equilibrium. The theoretical framework presented in this paper is illustrated with discussions of spin polarization in the contexts of force-detected nuclear-magnetic-resonance spectroscopy and magnetic-resonance force microscopy.

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I. INTRODUCTION

A limiting factor in many nuclear-magnetic-resonance (NMR) studies is the low thermal polarization of nuclear spins. In applied fields of several tesla, for instance, a nuclear-spin system must be cooled to millikelvin temperatures for the thermal polarization P to be of order unity, and at such low temperatures, the spin-lattice interactions which restore spins to thermal equilibrium between transients become "frozen out," yielding impractically long relaxation times [1]. Nonequilibrium methods for hyperpolarizing nuclear spins have widely applied [2–11], but the problem of long relaxation times at low temperatures has prevented the use of refrigeration as a practical method of achieving high levels of polarization for NMR applications.

A relaxation mechanism which does not depend on lattice temperature is spontaneous emission by the spins. Since the time constant for spontaneous emissions by a nuclear spin into free space is many orders of magnitude larger than the time available for NMR experiments [12], however, spontaneous emission normally makes a negligible contribution to relaxation. Enhancing the emission rate by coupling spins to an inductive resonator has enabled the detection of emitted energy in macroscopic samples in the high-temperature limit [13,14], but the enhancement provided by the resonator still yielded relaxation time constants far too long to be relevant for NMR applications.

Since scaling down the resonator to nanoscale can increase the spin-resonator coupling constant by orders of magnitude, we have studied the question of whether a cold nanoscale resonator could efficiently relax spins to thermal equilibrium with the resonator. A natural candidate for this investigation is a magnetic mechanical oscillator since these have proven to be sensitive NMR detectors of microscale samples. Mechanical detectors have been used in a variety of NMR methods, including imaging in a field gradient by means

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of magnetic-resonance force microscopy (MRFM) [15,16], NMR spectroscopy in a nominally homogeneous magnetic field [17,18], and multidimensional experiments that encode spectral and spatial information during distinct portions of each transient [19]. In particular, MRFM with a resolution of <10 nm has been demonstrated [16,20]. In the experiments which use a mechanical oscillator as a detector, the mechanical frequency has so far been orders of magnitude away from the spins' Larmor frequency, and modulation of the sample's spin dipole by means of radiofrequency (rf) fields has been required to produce a resonant interaction between the spins and the mechanical oscillator. Coupling the spins' Larmor precession to the resonant mechanical motion of nanoscale oscillators has been proposed [15,18,21], however, and resonator-enhanced spontaneous emission has been proposed as a substitute for spin-lattice relaxation between mechanically detected transients [21]. A calculation for a nanoscale torsional harmonic oscillator suggests the possibility of resonator-induced relaxation to polarization $P \sim 1$ with a rate constant $\sim 1\ \mathrm{s}^{-1}$ in the low-temperature limit [21].

The current paper provides a theoretical framework for the study of resonator-induced nuclear-spin polarization. Section II derives an interaction-frame Hamiltonian for the spin-resonator system at two different levels of approximation. The torsional mechanical resonator proposed in Ref. [21] is used for purposes of visualization, but the derivation can easily be adapted to the cases where a translational mechanical resonator or an inductive resonator is coupled to the spins. Section III presents equations of motion for the spin density matrix and the longitudinal spin component $\langle I_z \rangle$ during resonator-induced relaxation. The higher-order Hamiltonian is found to introduce negligible corrections to the master equation, which is dominated by rate processes that drive each manifold of definite spin angular momentum toward the temperature of the resonator. The physical interpretation of the equation governing spontaneous emission is discussed. The possibility of using an inductive resonator to polarize spins is considered, and it is shown that an exceptionally pure nanoscale coil would be required for efficient polarization. A semiclassical model of the spin-resonator system is introduced, and certain predictions of the semiclassical model are compared with the corresponding predictions of the quantum model. In particular, it is shown that the semiclassical model correctly describes the commonly observed phenomenon of radiation damping (i.e., the rotation of the spin dipole into alignment with the static field due to the back-action of the resonator), but fails to correctly describe the resonator-induced polarization of a spin 1/2.

In the simplest model of the polarization process, all spins experience the same field, and spin angular momentum is conserved by the spin-resonator interaction. This symmetry prohibits the spins from relaxing to thermal equilibrium with the resonator [21,22]. The 'trapping" of the spins away from full thermal equilibrium is associated with the development of spin-spin correlations that decrease the magnitude of the transverse spin fluctuations and thereby diminish the rate of spontaneous emission into the resonant mode. In Sec. IV, the semiclassical model is used to visualize the way in which these correlations develop: The interaction of many spins with a single resonator can be considered to introduce an indirect spin-spin interaction. The time needed for the development of spin correlations due to this indirect interaction is characterized.

Section V discusses the two ways in which the many-body secular spin Hamiltonian H_{spin} can affect the polarization process: (1) By modifying the structure of the spin-spin correlations in the energy eigenstates, and (2) by splitting the degeneracy within a manifold of energy eigenstates so that zero-frequency off-diagonal terms in the density matrix are converted to oscillating coherences. Shifting the frequencies of these coherences sufficiently far from zero suppresses the development of resonator-induced correlations within the manifold during polarization from a totally disordered state. The modification of the spin-spin correlations by means of either mechanism affects the strength of the fluctuating spin dipole that drives the resonator and donates energy to it. To first order, a perturbation in the spin Hamiltonian can affect the polarization process only through the second mechanism. The two mechanisms are illustrated by considering the way in which the polarization process is modified if either the homonuclear dipolar Hamiltonian H_D or the chemical-shift Hamiltonian H_{CS} is "turned on."

In Sec. VI, we study in greater detail the way in which H_{CS} modifies the resonator-induced polarization of a system of spins 1/2. If couplings between product-state populations and coherences are averaged to zero by H_{CS}, then $\langle I_z \rangle$ relaxes exponentially to thermal equilibrium, regardless of the initial spin state, and each spin can be regarded as relaxing independently of the others. For a system of isochronous spins, however, the spin-resonator interaction induces the development of zero-quantum operators that have off-diagonal matrix elements between product states differing by two spin flips. The trapping of the spin system away from thermal equilibrium is due to the presence of such terms, which constitute a nonlocal spin order. The trapping of this spin order is associated with the fact that certain linear combinations $\sum c_i |a_i\rangle$ of product states cannot relax because the sum of the probability amplitudes transferred from the states $|a_i\rangle$ to a lower-energy state $|b\rangle$ is zero. In the limit where the resonator temperature approaches 0 K, each trapped spin state is the ground state of a manifold of the total spin angular momentum. If H_{CS} splits the energy degeneracy of certain product states then the symmetry of angular momentum conservation is broken and the spins relax independently to thermal equilibrium.

Section VII considers the case where H_{CS} and H_D are both present. In two-spin and three-spin systems for which $H_D \gg H_{\mathrm{CS}}$, the symmetry of angular-momentum conservation is not fully broken by the spin Hamiltonian, and the population of certain states is therefore still trapped away from the ground state. Simulations of resonator-enhanced spontaneous emission suggest that as the number of spins is increased, the Hamiltonian $H_D + H_{\mathrm{CS}}$ becomes increasingly effective in coupling manifolds of different angular momentum and thereby facilitating relaxation to thermal equilibrium. In particular, the presence of H_{CS} in systems of a few dipole-dipole coupled systems tends to disrupt trapping and accelerate longitudinal relaxation by increasing the emission rates of weakly emitting eigenstates.

The system used throughout most of this paper for illustration of the theoretical results has a spin sample mounted

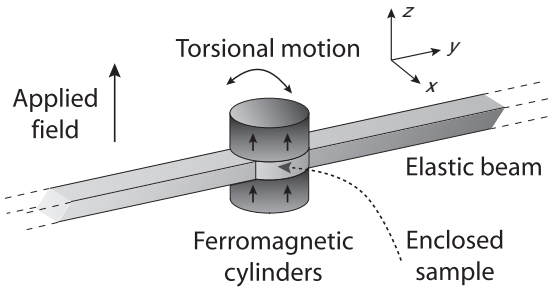

FIG. 1. Prototypical resonator design proposed in Ref. [21] for NMR spectroscopy of nanoscale samples. The sample is "sandwiched" between magnetic cylinders and rotates with the sandwich about the torsional beams. The nuclear-spin dipole couples to the oscillating transverse field generated by the cylinders.

on a torsional resonator, with all degrees of freedom of the spin-resonator system cooled to millikelvin temperatures. Section VIII considers resonator-induced polarization for two additional systems: a magnetic-resonance force microscope that uses a strong field gradient to image the sample, and a warm sample interacting with a mechanical mode that is cooled externally (e.g., by resolved-sideband cooling [23] or feedback cooling [24,25]).

The simulation methods used for this paper are discussed in Sec. IX.

II. HAMILTONIAN

We begin by obtaining the interaction-frame Hamiltonian at two different levels of approximation for a system consisting of a torsional mechanical resonator coupled to a collection of isochronous spins that interact only with the resonator. Notation will be defined using Fig. 1, which shows a resonator prototype designed for use in force-detected NMR spectroscopy of nanoscale samples [21]. The figure shows a "magnetic sandwich" that consists of two ferromagnetic cylinders and a disk of silicon that separates them, with the sample placed in a hollow space in the center of the silicon disk. The sandwich encloses an elastic beam, and the beam and sandwich together undergo torsional oscillations at fundamental frequency ω_h about the beam's long axis, labeled as the y axis in the figure. The coordinate θ is defined as the angular displacement of the sandwich axis from the equilibrium orientation, which will be assumed to coincide with the direction of an applied field defining the laboratory z axis. Since the motion of the ferromagnetic cylinders modulates the magnetic field at the spins, the resonator is coupled to the spins, and the coupling does not depend on the presence of a field gradient at the sample.

Let $\mathbf{B}(\theta)$ denote the field at the spins, which includes contributions from both the applied field and the field of the resonator. The Hamiltonian of the spin-resonator system is written in units of rad/s as

$$H = -\gamma \mathbf{I} \cdot \mathbf{B}(\theta) + H_{\rm osc}, \tag{1}$$

where $H_{\rm osc}$ is the Hamiltonian for the torsional harmonic oscillator, γ is the gyromagnetic ratio, and $\mathbf{I}$ is the spin angular-momentum operator, summed over all the spins. For small mechanical motions, $\mathbf{B}(\theta)$ can be approximated to first order in θ. In the absence of hysteresis, the resonator's symmetry dictates that

$$B_x(\theta) = -B_x(-\theta), \tag{2a}$$
$$B_y(\theta) = 0, \tag{2b}$$
$$B_z(\theta) = B_z(-\theta), \tag{2c}$$

regardless of the detailed way in which the magnetization of the cylinders evolves during the torsional oscillations. It follows that the first-order approximation to $\mathbf{B}(\theta)$ is

$$B_x(\theta) \approx \frac{dB_x}{d\theta}\theta, \tag{3a}$$
$$B_z(\theta) \approx B_z \equiv B_0, \tag{3b}$$

where we have simplified the notation by letting B_z and $dB_x/d\theta$ stand for $B_z(0)$ and $(dB_x/d\theta)(0)$, respectively. At this level of approximation, the Hamiltonian is

$$H = V + H_0,$$

where the interaction term is

$$V = \left(-\gamma \frac{dB_x}{d\theta}\right) I_x \theta, \tag{4}$$

and where

$$H_0 = \omega_0 I_z + H_{\rm osc}, \tag{5}$$
$$\omega_0 = -\gamma B_0. \tag{6}$$

Note that although Fig. 1 was included for purposes of visualization, Eq. (4) holds more generally as a first-order description of the coupling between spins and a torsional mechanical resonator having the symmetries expressed by Eqs. (2a) through (2c).

Making the substitutions

$$\theta = \sqrt{\frac{\hbar}{2I_h\omega_h}}(a + a^\dagger),$$
$$I_x = \frac{1}{2}(I_+ + I_-) \tag{7}$$

in Eq. (4) yields

$$V = g(I_+ a^\dagger + I_- a + I_+ a + I_- a^\dagger), \tag{8}$$

$$g = \frac{-\gamma}{2}\sqrt{\frac{\hbar}{2I_h\omega_h}}\frac{dB_x}{d\theta}, \tag{9}$$

where I_h is the oscillator's moment of inertia, I_+ and I_-, respectively, represent the raising operator and lowering operator summed over all the spins, and $a^\dagger$ and a, respectively, represent the raising operator and the lowering operator for the mechanical oscillator. Switching to the interaction frame which transforms away H_0 and using the resonance condition

$$\omega_h = -\omega_0 \tag{10}$$

to make the rotating-wave approximation yields

$$H_1 = g(I_+ a^\dagger + I_- a), \tag{11}$$

where we have simplified the notation by neglecting to distinguish between laboratory-frame operators and interaction-frame operators. Equation (10) assumes $\gamma > 0$ and incorporates the NMR convention that the time-averaged field at the spins points along the positive z axis; together, these imply that $\omega_0 < 0$, consistent with Eq. (10). For spins with $\gamma < 0$, the resonance condition $\omega_h = \omega_0$ gives an interaction Hamiltonian $H_1 = g(I_+a + I_-a^\dagger)$. Regardless of the sign of γ, however, the two product operators contributing to H_1 each exchange a quantum between spins and resonator. (For simplicity, $\gamma > 0$ will be assumed throughout this paper.)

Note that the use of the rotating-wave approximation is justified in the case where

$$|g| \ll |\omega_0|, \tag{12}$$

as can be verified by using the Magnus expansion [26] to calculate corrections to the average Hamiltonian H_1. Since the lowest-order correction to H_1 is smaller than H_1 by a factor of order g/ω_0, our analysis is valid in the regime where Eq. (12) holds (i.e., in the regime where H_0 effectively averages the nonresonant components of the interaction).

The use of the first-order expressions (3a) and (3b) yields a model in which B_z does not vary as the mechanical resonator moves. The model excludes the physical effects caused by fluctuations in B_z (e.g., resonator fluctuations cannot cause dephasing of the transverse dipole over the statistical ensemble). To obtain a model that includes such effects, and, more generally, to characterize the errors associated with approximating the field to first order in θ, we replace Eqs. (3a) and (3b) with second-order equations. Since Eq. (2a) implies that

$$\frac{d^2B_x}{d\theta^2} = 0$$

at $\theta = 0$, only the z component of the field changes when we move to this higher order of accuracy. The average Hamiltonian in the interaction frame becomes $H_1 + H_2$, where

$$\begin{aligned} H_2 &= wI_z(a^\dagger a - n_{\mathrm{th}}), \\ w &= -\gamma\frac{\hbar}{2I_h\omega_h}\frac{d^2B_z}{d\theta^2}, \end{aligned} \tag{13}$$

with

$$n_{\mathrm{th}} = \frac{1}{\exp(\hbar\omega_h/k_BT_h) - 1}$$

the thermal number of quanta in the resonator. Note that the Larmor frequency ω_0 depends on n_{th}:

$$\omega_0 = -\gamma B_z + w(n_{\mathrm{th}} + 1/2). \tag{14}$$

The relation between ω_0 and n_{th} given by Eq. (14) arises because the time-averaged value of the field depends on the resonator's thermal motion. In the case where $d^2B_z/d\theta^2 < 0$, for instance, the value of B_z is greatest when the resonator is in equilibrium position, and motion away from equilibrium decreases B_z. An increase in n_{th} corresponds to a larger average thermal displacement away from equilibrium and a resulting decrease in the time-averaged field. Fluctuations in $a^\dagger a$ away from n_{th} cause fluctuations in the longitudinal field at the spins, and these fluctuations survive averaging by H_0 in the interaction frame.

In Sec. III C 1, we show that $|w| \ll |g|$ for the example resonator, and that, more generally, the coupling constants for kth-order interactions decrease very rapidly with increasing k in the regime where $\sqrt{\hbar/2I_h\omega_h} \ll 1$.

III. EQUATIONS OF MOTION

A. Reduced master equation for the spins

Since H_1 has the form of the Jaynes-Cummings Hamiltonian, which governs the interaction between two-level atoms and a single resonant mode of the electromagnetic field [27], the evolution governed by H_1 can be characterized using results available in the literature. If a single spin 1/2 interacts with an undamped resonator, for instance, the initial state with the spin in its excited state and n quanta in the resonator evolves by periodically exchanging a quantum between the spin and the resonator at Rabi frequency $2g\sqrt{n+1}$ [27]. When N excited spins interact with an undamped resonator, initially in its ground state, excitation is transferred between the spins and resonator with a "quasiperiod" of order $1/(g\sqrt{N})$ [28,29]. In the presence of a thermal bath that weakly damps the resonator, the oscillations decay as quanta are dissipated from the resonator [28,29]. Increasing the strength of the resonator damping eventually suppresses the oscillations and allows the resonator to be treated as a bath that damps the spins, with the spin evolution described by a reduced master equation that does not explicitly include the resonator's degrees of freedom [28,29]. In the limit where the resonator temperature $T_h \to 0$ K, the condition for the use of a reduced master equation is

$$g\sqrt{N} \ll 2/\tau_h,$$

where τ_h is the time constant for the decay of the mechanical displacement in the absence of coupling to the spins [30].

The reduced master equation for a system of spins 1/2 in the limit of strong resonator damping is [28]

$$\frac{d\rho}{dt} = -i[H_{\mathrm{spin}},\rho] + \Lambda\rho, \tag{15}$$

where the spin-relaxation superoperator Λ is given by

$$\begin{aligned} \Lambda\rho = {} & R_0(n_{\mathrm{th}}+1)\left(I_+\rho I_- - \tfrac{1}{2}[I_-I_+,\rho]_+\right) \\ & + R_0n_{\mathrm{th}}\left(I_-\rho I_+ - \tfrac{1}{2}[I_+I_-,\rho]_+\right), \end{aligned} \tag{16}$$

with

$$R_0 = 2g^2\tau_h. \tag{17}$$

In Eq. (15), H_{spin} is the many-body secular spin Hamiltonian, expressed in the interaction frame in which the Hamiltonian H_0 of Eq. (5) has been eliminated, and all spins are assumed to have the same coupling to the resonator. The spin-lattice relaxation rate (e.g., due to phonons) has been assumed to be negligible. Equation (15) is derived by considering an undamped system of atoms that interact with a damped harmonic mode. In the low-temperature limit, where spin-lattice relaxation is "frozen out," Eq. (15) can be used to investigate relaxation due to the spin-resonator interaction H_1,

which is modulated by the thermal and quantum fluctuations of the harmonic mode.

Note that Eq. (15) is obtained by adding the term $-i[H_{\rm spin},\rho]$ to a relaxation superoperator derived under the assumption that $H_{\rm spin}=0$. This is valid if the resonator's ring-down time τ_h is short on the time scale of the evolution associated with $H_{\rm spin}$. The matrix elements of a relaxation superoperator can, in general, be evaluated by using second-order perturbation theory to write an approximate expression for the evolution occurring during a time step Δt that is long compared to the correlation time of the reservoir [31]. If the evolution governed by $H_{\rm spin}$ is sufficiently slow that it can be approximated by second-order perturbation theory during $\Delta t \gg \tau_h$, then the evaluation of the superoperator for the reduced master equation is unaffected by the presence of $H_{\rm spin}$. Our use of Eq. (15) to study resonator-induced polarization is thus limited to the regime in which the spectral width of resonator fluctuations is broad compared to the spectrum of $H_{\rm spin}$. As with the typical inductive circuits used for NMR, the case where the bandwidth of the resonator is broad compared to the NMR spectral width leads to simplifications.

Appendix A provides generalizations of Eq. (15). The same master equation is derived for a system of spins I, without the limitation $I=1/2$. Equations (A3) and (A4) give the reduced master equation governing a spin system in which an off-resonant mechanical mode is inducing relaxation. The case where $H_{\rm spin}$ has a spectral width comparable to or larger than the resonator bandwidth is also considered, and it is shown that a broad spectrum of spin interactions will shift some single-quantum transitions out of resonance, diminishing or eliminating the enhancement to spontaneous emission for these transitions. The relaxation superoperator associated with the Hamiltonian H_2 of Eq. (13) is derived, and it is shown that the contribution made by H_2 to the relaxation is smaller than the contribution associated with H_1 by a factor of $\sim(n_{\rm th}+1)w^2/g^2$. In Sec. III C 1, this ratio is shown to be negligible for the example resonator over a wide range of temperatures.

B. Equation of motion for $\langle I_z\rangle$

Equation (15) can be used to obtain an equation of motion for $\langle I_z\rangle$:

$$\frac{d}{dt}\langle I_z\rangle = -2R_0 n_{\rm th}\langle I_z\rangle + R_0\langle I_-I_+\rangle, \tag{18}$$

where

$$\langle I_-I_+\rangle = \left\langle I_x^2+I_y^2-I_z\right\rangle.$$

$H_{\rm spin}$ does not appear in Eq. (18) due to the fact that its commutator with I_z is zero. The spin Hamiltonian contributes indirectly to the relaxation of $\langle I_z\rangle$, however, by affecting the evolution of $\langle I_-I_+\rangle$. Note that Eq. (18) holds both in the interaction frame where H_0 has been eliminated and in the laboratory frame since its form is not changed by the transformation between these frames.

Since the Hamiltonian H_1 exchanges quanta between the spins and the resonator, Eq. (18) can be interpreted as characterizing the emission by the spins into the resonant mode and the absorption from it. The contributions of spontaneous and stimulated transitions can be distinguished by considering the limit $T_h\to 0$ K, where spontaneous emission is the only relaxation mechanism. Since $n_{\rm th}=0$ in this limit, the term proportional to $n_{\rm th}$ is associated with stimulated transitions; as expected, these transitions drive $\langle I_z\rangle$ toward zero. The relaxation of $\langle I_z\rangle$ due to spontaneous emission into a resonator at temperature $T_h=0$ K is governed by [32]

$$\frac{d}{dt}\langle I_z\rangle = R_0\langle I_-I_+\rangle \tag{19a}$$

$$= -R_0\langle I_z\rangle + R_0\left\langle I_x^2+I_y^2\right\rangle. \tag{19b}$$

Different physical interpretations of the mechanism of spontaneous emission exist in the literature [33–39], and the interpretations attached to Eqs. (19a) and (19b) depend on one's preferred interpretation for the mechanism of spontaneous emission. The equations of motion for an atom interacting with a radiation field can be arranged in such a way that the vacuum does not contribute directly to the evolution of the atom [36], and so spontaneous emission can be interpreted as resulting solely from the radiation reaction [33]. For the spin-resonator system, the analog of the radiation reaction is driving of the cold resonator by the transverse spin dipole. Note that even in the case where

$$\langle I_x\rangle = \langle I_y\rangle = 0,$$

the transverse dipole in general fluctuates about its mean value, and the resonant spectral component of this fluctuating dipole will drive the resonator. One can therefore adopt the point of view that the sole mechanism for spontaneous emission by a disordered spin system is relaxation to the ground state by damping of the transverse spin fluctuations. Under this interpretation, Eq. (19a) implies that I_-I_+ characterizes these fluctuations, and it is natural to consider I_-I_+ a variance or noise power of the complex transverse spin I_+.

An alternative arrangement of the equations of motion for an atom interacting with a radiation field suggests that vacuum fluctuations and the radiation reaction both contribute to spontaneous emission [36,37], and we will adopt this point of view in our discussion of resonator-induced relaxation. The resonator's zero-point fluctuations in general stimulate both the absorption and emission of energy by the spins, while the instantaneous transverse spin dipole, which in general includes a contribution both from the mean dipole and from spin fluctuations, drives the resonator and transfers energy to it. For a single spin 1/2, these two mechanisms for energy transfer contribute equally to spontaneous emission when the spin is in the excited state but cancel when it is in the ground state [39].

More generally, the terms $R_0\langle I_z\rangle$ and $R_0\langle I_x^2+I_y^2\rangle$ in Eq. (19b) can be interpreted as characterizing the contributions to spontaneous emission associated with zero-point fluctuation and with the driving of the resonator by the transverse spin dipole, respectively. The magnitude of these two contributions depends on the spin state. In the case where a large number N of spins are oriented in the transverse plane, we have $\langle I_x^2+I_y^2\rangle \gg \langle I_z\rangle$, and the driving of the resonator by the mean transverse dipole makes the dominant contribution to $d\langle I_z\rangle/dt$ in Eq. (19b). For a thermal system of spins 1/2 interacting with a resonator at temperature $T_h=0$ K, the mean

transverse dipole is zero, and it is the spin fluctuations that drive the resonator, rather than the mean dipole. Note that from this perspective, the contribution of spin fluctuations to spontaneous emission is temperature independent since $\langle I_x^2 + I_y^2 \rangle = N/2$ regardless of the spin temperature. This conclusion is consistent with the finding of the authors of Ref. [13] that the fluctuation-dissipation theorem predicts a temperature-independent injection of spin noise from a system of spins 1/2 into a resonant circuit. Since the contribution of vacuum fluctuations to $d\langle I_z \rangle/dt$ is proportional to $\langle I_z \rangle$, however, the net rate of spontaneous emission is temperature dependent.

In the case where only a single spin 1/2 is present, we have

$$I_x^2 = I_y^2 = 1/4,$$

and Eq. (18) reduces to

$$\frac{d}{dt}\langle I_z - \langle I_z \rangle_{\rm th} \rangle = -R_h \langle I_z - \langle I_z \rangle_{\rm th} \rangle, \tag{20}$$

where

$$\langle I_z \rangle_{\rm th} = \frac{1}{2} \tanh\left(-\frac{\hbar\omega_0}{2k_B T_h}\right)$$

is the mean value of I_z for a spin in thermal equilibrium at temperature T_h, and where

$$R_h = R_0(2n_{\rm th} + 1) \tag{21}$$

is the rate constant for the exponential relaxation of $\langle I_z \rangle$ to $\langle I_z \rangle_{\rm th}$. When multiple spins are present, however, the relaxation is generally not exponential due to the contribution of spin-spin correlations to the term

$$\left\langle I_x^2 + I_y^2 \right\rangle = \sum_i \sum_j \langle I_{ix} I_{jx} + I_{iy} I_{jy} \rangle. \tag{22}$$

In the case where the mean transverse dipole is zero, for example, the presence of spin-spin correlations in general modifies the transverse fluctuations that contribute to spontaneous emission.

C. Estimated magnitude of rate constants

1. *Example mechanical resonator*

The rate constant R_h defined by Eq. (21) characterizes the resonator-induced relaxation of $\langle I_z \rangle$. In estimating the magnitude of R_h we refer to a numerical example based on the resonator prototype pictured in Fig. 1. This resonator has a "magnetic sandwich" diameter 55 nm and height of 105 nm, consisting of two cylinders of soft ferromagnetic material separated by a silicon disk of thickness 25 nm. Each of the two elastic beams attached to the sandwich has a cross section 50 nm × 50 nm and length 1.75 μm. The resonator is assumed to be held at the temperature of $T_h = 10$ mK. For this example, the calculated rate constant is [21]

$$R_h = 1.3\ {\rm s}^{-1}.$$

This resonator can also be used to characterize the significance of the corrections to the master equation obtained by expanding the field to second order or higher in θ. As shown in Appendix A, the contribution made by H_2 to the relaxation superoperator is smaller than the contribution associated with H_1 by a factor of $\sim(n_{\rm th} + 1)w^2/g^2$, which depends on the ratio of $d^2B_z/d\theta^2$ to $dB_x/d\theta$. Finite-element software (MAXWELL 3D v11, Ansoft Corporation, Pittsburgh) was used to simulate the resonator's magnetic field, and it was found that the field at the spins $\mathbf{B}(\theta)$ could be approximated to second order in θ as

$$\mathbf{B}(\theta) = \mathbf{B}_a + B_h\left(\tfrac{3}{2}\theta, 0, 1 - \tfrac{3}{2}\theta^2\right), \tag{23}$$

where $\mathbf{B}_a$ is the applied field, which is directed along the z axis, and where $B_h = 1.1$ T is the magnitude of the resonator's contribution to the time-averaged field. It follows that

$$\frac{dB_x}{d\theta} = -\frac{1}{2}\frac{d^2B_z}{d\theta^2},$$

which gives

$$(n_{\rm th} + 1)\frac{w^2}{g^2} = (n_{\rm th} + 1)\frac{8\hbar}{I_h\omega_h}.$$

Using the calculated resonator parameters [21]

$$I_h = 6.3 \times 10^{-33}\ {\rm kg\ m^2},$$
$$\omega_h/2\pi = 630\ {\rm MHz},$$
$$n_{\rm th} = 0.05,$$

we find that

$$\frac{w^2}{g^2} \approx 10^{-11},$$

which is sufficiently small to render the contribution of H_2 to the master equation negligible over a wide range of temperatures.

The factor $\hbar/I_h\omega_h$ appears in the ratio w^2/g^2 because

$$\theta = \sqrt{\frac{\hbar}{2I_h\omega_h}}(a + a^\dagger)$$

was substituted into the series expansion of $\mathbf{B}(\theta)$ to find the resonant interactions that are not averaged to zero by the fast, unperturbed motion of the spins and the mechanical oscillator. In the full series expansion of the interaction Hamiltonian of Eq. (1), a resonant interaction H_u that is kth order in θ can be expressed in the form

$$H_u = g_u\, I_u\, a_1^u\, a_2^u, \ldots, a_k^u,$$

where

$$g_u \propto \left(\sqrt{\frac{\hbar}{2I_h\omega_h}}\right)^k \tag{24}$$

is a coupling constant, I_u is one of the a spherical-tensor spin operators I_+, I_-, I_z, and a_i^u is either a raising or lowering operator for the oscillator. A kth-order interaction thus involves k transitions by the oscillator, and it follows from Eq. (24) that in the regime where

$$\sqrt{\hbar/2I_h\omega_h} \ll 1, \tag{25}$$

the magnitude of the coupling constants for such processes decreases sharply with increasing k. It is because the example resonator satisfies Eq. (25) that the second-order Hamiltonian H_2 makes a negligible contribution to relaxation over a wide range of temperatures.

2. *Nanoscale inductive resonator*

It is natural to ask whether an inductive resonator could polarize spins as efficiently as a mechanical resonator. In considering this question, we note first that a Hamiltonian of the same form as H_1 can be derived for a system consisting of an LC circuit coupled to a collection of spins. The Hamiltonian for an LC circuit is [40]

$$H = \frac{p^2}{2L} + \frac{q^2}{2C},$$

where q is the charge, L is the inductance, C is the capacitance, and $p = L\dot{q}$ is the momentum conjugate to q. Arguments similar to those used in Sec. II show that the time-averaged interaction-frame Hamiltonian for the spin-resonator system has the same form as H_1, but with the coupling constant g of Eq. (11) replaced by

$$g_L = -\frac{\gamma}{2}\frac{\mu_0 n}{L}\sqrt{\frac{L\hbar\omega_L}{2}}, \tag{26}$$

where ω_L is the resonator frequency, and n is the number of turns per unit length of the solenoid generating the field. In the derivation of Eq. (26), the resonator's field at the spins is approximated as

$$\mathbf{B}(p) = \left(0, \frac{\mu_0 n}{L} p, 0\right).$$

Longitudinal relaxation of the spins is governed by the rate constant

$$R_L = 2g_L^2 \tau_L \left(2n_{\text{th}} + 1\right), \tag{27}$$

where the ring-down time of the LC circuit is

$$\tau_L = 2L/R, \tag{28}$$

with R the circuit resistance.

In comparing mechanical and inductive resonators, we first consider the way in which g^2 and g_L^2 scale with size. If the frequency is allowed to vary without constraint as the dimensions of the spin-resonator system are uniformly scaled, we find that

$$g^2 \propto \frac{1}{I_h \omega_h} \propto 1/r^4,$$

and

$$g_L^2 \propto \frac{n^2 \omega_L}{L} \propto 1/r^4.$$

However, if the external field that determines the Larmor frequency is held fixed during the scaling, with the harmonic suspension of the mechanical oscillator and the capacitance of the inductive oscillator adjusted to preserve the resonance between the oscillator and the spins, we obtain

$$g^2 \propto \frac{1}{I_h} \propto 1/r^5,$$

and

$$g_L^2 \propto \frac{n^2}{L} \propto 1/r^3.$$

At a given frequency, the strength of the spin-resonator coupling depends more strongly on size if the resonator is mechanical.

The mechanical-polarization rate constant R_h depends on the resonator ring-down time τ_h as well as the coupling strength g, and a quantitative prediction of τ_h is not possible. A detailed comparison of R_h and R_L is therefore difficult. We can, however, make simple estimates which suggest that an extremely pure conductor would be required for efficient inductive cooling at mK temperatures. Starting from the example inductive coils used in Ref. [41] to compare the NMR detection sensitivity of mechanical oscillators and inductive oscillators, we estimate R_L for scaled-down, low-temperature inductive resonators. The example coils have six turns, with a length-to-diameter ratio of 0.7, and with a spacing between each loop of wire that is equal to the wire radius. A proximity factor of 3 is used in estimating the coil resistance [42]. Cooling an exceptionally pure conductor to a temperature of a few Kelvins or below can increase its conductivity by a factor of up to 10^6 [43]. If the example coils of Ref. [41] are scaled down to have a length of 60 nm, and if the conductivity is assumed to be six orders of magnitude greater than that of room-temperature copper, we obtain

$$\begin{aligned} R_L &\approx 2g_L^2 \tau_L \\ &= (\gamma \mu_0 n)^2 \frac{\hbar \omega_L}{2R} \\ &\approx 0.1 \text{ s}^{-1}, \end{aligned}$$

where $\omega_L/2\pi = 600$ MHz. The cooling of nuclear spins by a nanoscale inductive resonator could therefore be experimentally relevant if an exceptionally pure conductor is used.

D. Semiclassical equation

This section introduces a semiclassical model of the spin-resonator system. A collection of "semiclassical spins" interact only with a classical mechanical oscillator and experience the same field $\mathbf{B}(\theta)$. The semiclassical spin vector $\boldsymbol{\mathcal{I}}$ is defined to be a vector of variables rather than operators: each spin component has a definite value at all times. The interaction between the spins and the resonator is governed by the potential energy

$$W = -\boldsymbol{\mu} \cdot \mathbf{B}(\theta),$$

where $\boldsymbol{\mu} = \gamma\hbar\boldsymbol{\mathcal{I}}$ is the magnetic dipole, summed over all the spins. With the semiclassical spin angular momentum defined as $\hbar\boldsymbol{\mathcal{I}}$, it follows that [43]

$$\frac{d}{dt}\boldsymbol{\mathcal{I}} = \gamma \boldsymbol{\mathcal{I}} \times \mathbf{B}, \tag{29}$$

and that the torque exerted on the resonator by the spins is

$$-\frac{\partial W}{\partial \theta} = \gamma\hbar \frac{dB_x}{d\theta}\mathcal{I}_x, \tag{30}$$

where $\mathbf{B}(\theta)$ is given by Eqs. (2b), (3a), and (3b), as in the quantum-mechanical model. If only a single spin is present, the precession of $\boldsymbol{\mathcal{I}}$ about the large static field B_z causes $\mathcal{I}_x$ to vary sinusoidally at the mechanical frequency $\omega_h = |\omega_0|$. The mechanical oscillator thus responds to a resonant torque exerted by the spin, which in turn nutates about the resonant rotating component of the oscillator's transverse field. In a thermal system of many spins, for which $\langle \mathcal{I}_x \rangle = \langle \mathcal{I}_y \rangle = 0$, the transverse dipole of each spin exerts a driving torque on the

resonator and donates energy to it independently. Although $\langle \mathcal{I}_x \rangle = \langle \mathcal{I}_y \rangle = 0$, the net transverse dipole fluctuates as the spins precess about the z axis, and the fluctuating net dipole drives the resonator.

Appendix B derives an equation of motion for $\langle \mathcal{I}_z \rangle$ for a system of N spins, where the average is taken over a statistical ensemble:

$$\frac{d}{dt}\langle \mathcal{I}_z \rangle = -2R_0 \frac{\langle E_h \rangle}{\hbar\omega_h}\langle \mathcal{I}_z \rangle + R_0\langle \mathcal{I}_x^2 + \mathcal{I}_y^2 \rangle. \tag{31}$$

Here $\langle E_h \rangle$ is the mean thermal energy of the resonator, with the energy at $T_h = 0$ K taken as the origin of the energy scale. For purposes of comparison with Eq. (31), we write the corresponding quantum mechanical equation in the form

$$\frac{d}{dt}\langle I_z \rangle = -2R_0 \frac{\langle E_h \rangle}{\hbar\omega_h}\langle I_z \rangle + R_0\langle I_x^2 + I_y^2 - I_z \rangle. \tag{32}$$

A comparison of Eqs. (31) and (32) shows a strong formal similarity between the quantum and semiclassical equations and suggests that certain aspects of the relaxation can be understood using the semiclassical model. For example, the semiclassical model is used in Sec. IV to visualize the way in which an indirect spin-spin interaction arises due to the coupling of many spins to a single resonator.

Perhaps more interesting than the formal similarity between the two equations are the significant differences between the evolution that they predict. Note first that the passage from a quantum system to a semiclassical system causes the loss of the term $-R_0\langle I_z \rangle$, as might be expected, since this term can be interpreted as characterizing the contribution of zero-point mechanical fluctuations to spontaneous emission. The contribution associated with driving by the transverse spin dipole is also different due to differences in the properties of the operator $I_x^2 + I_y^2$ and the variable $\mathcal{I}_x^2 + \mathcal{I}_y^2$; in particular, there are significant differences between quantum mechanical and semiclassical spin fluctuations. Consider, for example, a thermal system of spins 1/2 that begin to interact with a resonator at $T_h = 0$ K. If the spins are initially at infinite temperature (i.e., completely disordered), quantum mechanical spin fluctuations make a contribution

$$R_0\langle I_x^2 + I_y^2 \rangle = R_0 N/2$$

to $d\langle I_z \rangle/dt$. In the corresponding semiclassical system, the contribution of the transverse fluctuations to $d\langle \mathcal{I}_z \rangle/dt$ is

$$R_0\langle \mathcal{I}_x^2 + \mathcal{I}_y^2 \rangle = R_0 N/6.$$

At infinite spin temperature, therefore, a similar contribution is made by the semiclassical and quantum spin fluctuations. However, when all spins are oriented along either the positive or negative z axis (i.e., in the limiting cases where the initial spin temperature approaches zero from above or below, respectively), the semiclassical spins do not fluctuate, while the quantum spin fluctuations make the same contribution to $d\langle I_z \rangle/dt$ as at infinite temperature.

A striking feature of the semiclassical system is that since the spins all experience the same field, the evolution can be simply described as the precession of the entire spin system around the instantaneous field. Indeed, Eq. (29) implies that the derivative $d\boldsymbol{\mathcal{I}}/dt$ is perpendicular to $\boldsymbol{\mathcal{I}}$, and it follows that this equation describes a rotation of the vector $\boldsymbol{\mathcal{I}}$. The spin-resonator interaction can therefore only rotate the net spin dipole without changing its magnitude. (Note, however, that this argument does not prohibit a change in $\langle \mathcal{I}_x^2 + \mathcal{I}_y^2 + \mathcal{I}_z^2 \rangle$ for a statistical ensemble of semiclassical systems.) By way of contrast, the evolution of a quantum mechanical system of spins under the Hamiltonian $-\gamma \mathbf{I} \cdot \mathbf{B}(\theta)$ cannot in general be characterized as a simple rotation since the field $\mathbf{B}(\theta)$ is an operator rather than a classical variable.

The distinction between radiation damping (i.e., the rotation of a precessing spin dipole into alignment with the static field due to the resonator's back-action) and resonator-induced spin polarization can be clarified by observing that the semiclassical model correctly describes radiation damping but not the resonator-induced polarization of a spin 1/2. To obtain an equation of motion for $d\langle I_z \rangle/dt$ during radiation damping, we consider a large system of spins 1/2 for which the spins are sufficiently well aligned and the projection of the mean dipole onto the transverse plane is sufficiently large that $\langle I_x^2 + I_y^2 \rangle \gg \langle I_z \rangle$. Since thermal fluctuations of the resonator do not play an essential role in radiation damping, we can assume $T_h = 0$ K. Under these conditions, Eq. (18) can be expressed as

$$\frac{d}{dt}\langle I_z \rangle \approx R_0\langle I_x^2 + I_y^2 \rangle. \tag{33}$$

A similar equation is obtained from the semiclassical model. Setting $\langle E_h \rangle$ to zero in Eq. (31) yields

$$\frac{d}{dt}\langle \mathcal{I}_z \rangle = R_0\langle \mathcal{I}_x^2 + \mathcal{I}_y^2 \rangle. \tag{34}$$

It is straightforward to verify that Abragam's equation of motion for radiation damping [44] can be obtained from Eqs. (33) or (34) if $R_0 = 2g^2\tau_h$ is replaced by the corresponding constant $2g_L^2\tau_L$ for an inductive resonator, where g_L and τ_L are given by Eqs. (26) and (28), respectively. We conclude that the semiclassical model is consistent with earlier models of radiation damping. If the large system of aligned spins is replaced by a single spin 1/2, however, the semiclassical evolution is still governed by Eq. (34), while the quantum mechanical evolution is governed by Eq. (19a), which can be written as

$$\begin{aligned}\frac{d}{dt}\langle I_z \rangle &= R_0\langle I_x^2 + I_y^2 - I_z \rangle \\ &= R_0(1/2 - \langle I_z \rangle).\end{aligned} \tag{35}$$

In contrast to Eq. (34), the quantum mechanical equation predicts that $\langle I_z \rangle$ will relax exponentially to 1/2, regardless of the initial spin state. Note, for example, that the evolution of $\langle I_z \rangle$ is the same for a spin initially oriented in the transverse plane as for one at infinite temperature since the initial value of $\langle I_z \rangle$ is the same in these two cases. Note as well that Eq. (35) predicts that the maximum possible value of $d\langle I_z \rangle/dt$ occurs in the case where the spin is oriented along the negative z axis. By way of contrast, Eq. (34) has $d\langle \mathcal{I}_z \rangle/dt = 0$ if the spin is oriented along the negative z axis, while the maximum possible value of the derivative occurs if the spin lies in the transverse plane.

IV. TRAPPING OF THE SPIN POPULATION

Although a single spin 1/2 will relax exponentially to thermal equilibrium with the resonator, a collection of spins

1/2 coupled to a cold resonator by the Hamiltonian H_1 will not in general relax to a thermal state [21,22]. Since the Hamiltonian H_1 commutes with $\mathbf{I}^2$, spin angular momentum is conserved during the relaxation if the spin Hamiltonian does not break this symmetry. Unless the initial spin state has the same total angular momentum as the state corresponding to thermal equilibrium with the resonator, the conservation of angular momentum prohibits the spins from relaxing to thermal equilibrium.

Consider an example where $H_{\rm spin} = 0$ and where N spins 1/2 interact with a resonator at temperature $T_h = 0$ K. The spin system contains only one angular-momentum manifold with $I = N/2$, and the ground state is the low-energy state of this manifold. Since relaxation governed by H_1 does not transfer the population between angular momentum manifolds of different I, the spins cannot relax to the ground state if the initial spin state has a population in any of the angular momentum manifolds with $I < N/2$. Rather, the initial population of each angular momentum manifold will be transferred to the lowest-energy state of the manifold and remain "trapped" in this state [21,22]. In particular, if the initial distribution of N spins 1/2 is completely disordered, with all states of all angular momentum manifolds equally populated, then the spins will relax to a polarization of [21]

$$P_{\rm trap} = \frac{1}{2^{N-1}N}\sum_{J}^{N/2}\frac{N!(2J+1)^2}{(N/2+J+1)!(N/2-J)!} \approx \sqrt{2/N}, \quad N \gg 1. \tag{36}$$

The trapping of the spin system is associated with correlations which develop between spins due to their interaction with a single resonator [22]. For an initially disordered spin system coupled to a resonator at $T_h = 0$ K, the contribution of resonator-induced spin-spin correlations to trapping can be highlighted by writing Eq. (18) as

$$\frac{d}{dt}\langle I_z - N/2\rangle = -R_0\langle I_z - N/2\rangle + R_0\langle I_x^2 + I_y^2 - N/2\rangle. \tag{37}$$

In the absence of any correlations between the spins, $\langle I_x^2 + I_y^2 - N/2\rangle = 0$ in the second line of Eq. (37), and $\langle I_z\rangle$ relaxes exponentially toward $N/2$. The equilibrium value $\langle I_z\rangle = N/2$ corresponds to a state in which the transfer of energy away from the spins due to the transverse fluctuations of the uncorrelated spins is exactly balanced by the tendency of zero-point fluctuations to drive the spins toward infinite temperature. The development of spin-spin correlations during resonator-induced relaxation decreases the magnitude of the transverse fluctuations, however, yielding $\langle I_x^2 + I_y^2 - N/2\rangle < 0$ and slowing down the transfer of energy away from the spins. The spins relax to a steady state in which the outward flow of energy due to these weakened transverse fluctuations is balanced by the inward flow of energy due to zero-point fluctuations. This steady state has $\langle I_z\rangle < N/2$ since the inward energy flow associated with zero-point fluctuations is proportional to $\langle I_z\rangle$.

More generally, $R_0\langle I_x^2 + I_y^2 - N/2\rangle$ can be interpreted as the instantaneous contribution of spin-spin correlations to $d\langle I_z\rangle/dt$, regardless of the resonator temperature or the nature of the spin Hamiltonian. Equation (18) can be expressed as

$$\frac{d}{dt}\langle I_z\rangle = -R_h n_{\rm th}\langle I_z\rangle + R_0 N/2 + R_0\langle I_x^2 + I_y^2 - N/2\rangle. \tag{38}$$

Since the second line of Eq. (38) is zero in a system of uncorrelated spins 1/2, we can interpret this line as giving the instantaneous contribution associated with spin-spin correlations. The spin order associated with departures from independent-spin relaxation is thus

$$I_x^2 + I_y^2 - N/2 = \sum_{i<j}(I_{i+}I_{j-} + I_{i-}I_{j+}).$$

The semiclassical model introduced in Sec. III D can be used to visualize the way in which resonator-induced correlations develop, as well as to estimate the time needed for their development. Consider an example in which the classical resonator is at temperature $T_h = 0$ K. The resonator quickly achieves a steady-state response to torques exerted by all the spins since the resonator ring-down time is short on the time scale of spin relaxation. An indirect spin-spin interaction arises because the field at a given spin k includes a contribution from the resonator's steady-state response to driving by spin j. The torque acting on spin k due to the driving of the resonator by spin j can be interpreted as an indirect torque exerted on spin k by spin j, and the indirect torques which link each pair of spins cause the development of spin-spin correlations.

To quantify the strength of the indirect torques, we consider the interactions occurring in the semiclassical system during a time step Δt that is long compared to the resonator ring-down time but short compared to the spin-relaxation time. If the orientation of spin j at $t = 0$ is specified by the angles ϕ_j and α_j, with ϕ_j the azimuthal angle and α_j the angle between the spin and the z axis, then the resonator's steady-state motion during Δt is

$$\theta(t) = \frac{dB_x}{d\theta}\frac{\gamma\hbar\mathcal{I}\tau_h}{2I_h\omega_h}\sum_j \sin\alpha_j \sin(\omega_h t - \phi_j), \tag{39}$$

where $\mathcal{I}$ is the magnitude of the semiclassical spin vector associated with an individual spin, and where we have assumed that all spins experience the same field and precess at frequency $\omega_0 = -\omega_h$. [Equation (39) is obtained by summing the resonator's steady-state responses to the torques exerted by individual spins, with the torque calculated using Eq. (30).] The resonator's transverse field is given by the product $\theta(t)\,dB_x/d\theta$, and the contribution to this field associated with driving by spin j can be considered the effective field of spin j experienced by the other spins. The amplitude B_j of this field is

$$B_j = \left(\frac{dB_x}{d\theta}\right)^2\frac{\gamma\hbar\tau_h}{2I_h\omega_h}(\mathcal{I}\sin\alpha_j).$$

In a reference frame rotating about the z axis at the Larmor frequency of the spins, the resonant component of this field has magnitude $B_j/2$, and the precession frequency of spin k in a field of this magnitude is

$$\gamma B_j/2 = R_0\mathcal{I}\sin\alpha_j, \tag{40}$$

i.e., R_0 times the transverse component of spin j.

Equation (40) can be used to estimate the time needed for spin correlations to develop due to the spin-resonator coupling. Consider a statistical ensemble in which the transverse components of N semiclassical spins 1/2 are distributed randomly (i.e., the probability distribution of each azimuthal angle ϕ_j is flat and uncorrelated with α_j). In a frame rotating about the z axis at the Larmor frequency, we calculate the evolution of spin k under the indirect torques exerted by spins $j \neq k$. Define $\mathbf{B}'$ as the vector sum of the resonant transverse fields associated with driving of the resonator by spins $j \neq k$, and note that although the ensemble average $\langle \mathbf{B}' \rangle = \mathbf{0}$, the actual magnitude of this field for an arbitrary ensemble member can be estimated as the root-mean-square (rms) magnitude of $\mathbf{B}'$. Spin k will nutate at the frequency

$$\omega' = R_0 \bar{\mathcal{I}}_{\text{trans}} \sqrt{N-1}$$

in this rms field, where $\bar{\mathcal{I}}_{\text{trans}}$ is the rms magnitude of the transverse component of an individual spin. For a completely disordered system of $N \gg 1$ semiclassical spins 1/2, we have $\bar{\mathcal{I}}_{\text{trans}} = \sqrt{1/6}$, and the characteristic evolution time of each spin in the net field exerted indirectly by all of the other spins is

$$1/\omega' \approx (R_0 \sqrt{N/6})^{-1}. \tag{41}$$

By way of contrast, observe that for an initial state which has the $N \gg 1$ spins aligned in the transverse plane, the indirect torques add coherently, and the characteristic evolution time of a spin due to the indirect couplings is

$$1/\omega' \approx (R_0 N/2)^{-1}. \tag{42}$$

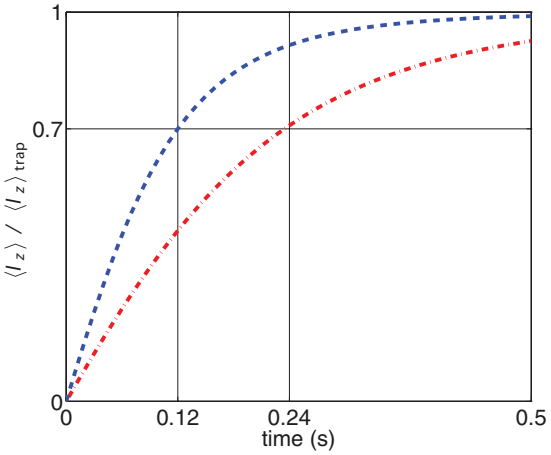

FIG. 2. (Color online) The dashed (blue) and dash-dotted (red) curves show the evolution of $\langle I_z \rangle$ in two systems of isochronous spins that interact only with the resonator and relax from an initially disordered state, with the respective systems having $N = 144$ and $N = 36$ spins. The curves are normalized to take the value 1 when the system has relaxed to its trapped state, and the value of $\langle I_z \rangle$ in this state is denoted by $\langle I_z \rangle_{\text{trap}}$. For both curves, the time $t = (R_0\sqrt{N/2})^{-1}$ corresponds to a point at which $\langle I_z \rangle$ has relaxed to about 70% of its value in the trapped state. For $N = 144$ and $N = 36$, these respective times are $t = 0.12$ s and $t = 0.24$ s. As in all simulations presented in this paper, the resonator temperature is $T_h = 0$ K, and the rate constant for resonator-enhanced spontaneous emission is $R_0 = 1\ \text{s}^{-1}$.

An estimate consistent with Eq. (41) can be obtained by an analysis based on the quantum mechanical equations (18) and (36), as shown in Appendix C. The time needed for the significant relaxation of $\langle I_z \rangle$ and $\langle I_x^2 + I_y^2 \rangle$ toward their trapped final values is estimated as

$$T_{\text{trap}} = (R_0 \sqrt{N/2})^{-1}. \tag{43}$$

Figure 2 presents the results of two quantum mechanical simulations that test this estimate. The dashed and dash-dotted curves show the evolution of $\langle I_z \rangle$ in two systems of isochronous spins that interact only with the resonator and relax from an initially disordered state, with the respective systems having $N = 144$ and $N = 36$ spins. The curves are normalized to take the value 1 when the system has relaxed to its trapped state. For both curves, the time $t = T_{\text{trap}}$ corresponds to a point at which $\langle I_z \rangle$ has relaxed to about 70% of its value in the trapped state. Although not shown in the figure, $\langle I_x^2 + I_y^2 - N/2 \rangle$ was found to relax to about 60% of its trapped-state value during the same time period.

V. EFFECT OF THE SPIN HAMILTONIAN ON RESONATOR-INDUCED POLARIZATION

In analyzing the way in which the secular spin Hamiltonian H_{spin} affects the process of spin polarization, we begin by writing a general expression for the master equation (15) in the interaction frame where H_{spin} has been eliminated, and we highlight two ways that a change in H_{spin} can modify this expression. (Note that unless otherwise specified, the term "interaction frame" will be used in the remainder of this paper to refer to the reference frame in which both H_0 and H_{spin} have been eliminated.) Let S denote the spin system and R the reservoir that damps the spins (i.e., the resonator and its thermal bath). The sets $\{|a\rangle\}$, $\{|\mu\rangle\}$ represent orthonormal bases of energy eigenfunctions for S and R, respectively; the product states $|a\rangle|\mu\rangle$ would be energy eigenstates in the absence of the spin-resonator coupling. The energy (in rad/s) of a state $|a\rangle$ is denoted by ω_a, and the Bohr frequencies of S by $\omega_{ab} = \omega_a - \omega_b$. The master equation governing the evolution of the interaction-frame spin density matrix ρ is [31]

$$\frac{d}{dt}\rho_{ab}(t) = \sum_{c,d} \exp[i(\omega_{ab} - \omega_{cd})t] \mathcal{R}_{abcd}\, \rho_{cd}(t), \tag{44}$$

where the coefficients $\mathcal{R}_{abcd}$ are constants. Each coefficient $\mathcal{R}_{abcd}$ can be expressed as a linear combination of terms having the form $A_1 A_2 G_{mn}$, where A_1 and A_2 are matrix elements of the laboratory-frame operators I_+ and I_-, and where G_{mn} is the Fourier component at Bohr frequency ω_{nm} of a resonator correlation function involving the interaction-frame operators a and $a^\dagger$ [31]. In the case where S consists of a single spin, for example, with ground state $|b\rangle = |+\rangle$ and excited state $|c\rangle = |-\rangle$, $\mathcal{R}_{bbcc}$ includes a contribution from the term

$$g^2 \langle c|I_-|b\rangle \langle b|I_+|c\rangle \int_0^\infty dt\, \langle a(t) a^\dagger(0) \rangle_{\text{th}} \exp(-i\omega_0 t),$$

which has the form $g^2 A_1 A_2 G_{cb}$, where $A_1 = \langle c|I_-|b\rangle$, $A_2 = \langle b|I_+|c\rangle$, and where the correlation function is $G(t) = \langle a(t) a^\dagger(0) \rangle_{\text{th}}$, with the subscript "th" denoting a thermal average over the reservoir.

The significance of a given spin interaction for the process of resonator-induced polarization can be studied by analyzing the way in which the interaction affects Eq. (44). Note that a perturbation H' in the spin Hamiltonian can affect the relaxation in two distinct ways: (1) By modifying the coefficients $\mathcal{R}_{abcd}$, and (2) by shifting the frequencies $(\omega_{ab} - \omega_{cd})$. In the regime considered in the paper, where the resonator bandwidth is large compared to the bandwidth of the NMR spectrum, a perturbation that shifts the eigenfrequencies ω_a without changing the eigenstates $|a\rangle$ will not change the coefficients $\mathcal{R}_{abcd}$. This follows from the fact that $\mathcal{R}_{abcd}$ is a linear combination of terms of the form $A_1 A_2 G_{mn}$: neither the matrix elements A_1, A_2 nor the frequency components G_{nm} of the resonator correlation functions are modified by shifts of the eigenfrequencies, provided the shifts are small compared to the spectral widths of the correlation functions. A perturbation of the eigenfrequencies can thus modify the relaxation only through the term $(\omega_{ab} - \omega_{cd})$, the frequency at which the relative phase of the laboratory-frame coherences $|a\rangle\langle b|$ and $|c\rangle\langle d|$ is modulated by H_{spin}. This laboratory-frame modulation of the relative phase appears in the interaction frame as an oscillation in the phase of the transfer from ρ_{cd} to ρ_{ab}, as can be seen by examining Eq. (44). As a typical example of the effect of such a perturbation, note that if the frequency difference $|\omega_{ab} - \omega_{cd}|/2\pi \ll |\mathcal{R}_{abcd}|$ is perturbed to a value much larger than $|\mathcal{R}_{abcd}|$, then the relaxation associated with the transfer from ρ_{cd} to ρ_{ab} will be suppressed since the perturbation H' will average the net transfer to zero.

Consider the case where the spin Hamiltonian contains two noncommuting terms H' and H'', with $H' \gg H''$. In analyzing this problem, we begin with a set of energy eigenstates of H', where any degenerate eigenstates are chosen to be zero-order eigenstates of the weak perturbation H''. "Turning on" the perturbation H'' cannot significantly affect this set of spin-energy eigenstates or the coefficients $\mathcal{R}_{abcd}$; indeed, it can affect the polarization process only by shifting the frequencies of off-diagonal terms and modifying the way in which H_{spin} averages transfers involving these terms.

More generally, we see that within an appropriately chosen energy eigenbasis of the dominant terms in the spin Hamiltonian, a weak perturbation cannot affect the polarization processes that depend solely on the direct transfer between the diagonal terms of the density matrix. Note as well that since resonator-induced relaxation is slow on the time scale of spin dynamics, transfers between diagonal and off-diagonal terms can only play a significant role in the polarization process if the frequency of an off-diagonal element ρ_{ab} is zero or close to zero (i.e., if the states $|a\rangle$ and $|b\rangle$ can be considered essentially degenerate). To first order, therefore, a perturbation can modify the polarization process only by shifting the frequencies of off-diagonal terms that are associated with a degeneracy among energy eigenstates. For a physical interpretation of how such frequency shifts affect the relaxation, note that if a system is initially in a totally disordered state, zero-frequency off-diagonal terms that develop during the relaxation correspond to resonator-induced spin order within a degenerate manifold. Frequency shifts that affect the polarization process can thus be interpreted as suppressing the development of resonator-induced correlations within such manifolds. By way of contrast, a strong perturbation that significantly changes the energy eigenstates will directly modify the structure of the correlations associated with the eigenstates. Regardless of whether a perturbation modifies the correlations directly or indirectly, however, the physical effect is to modify the strength of the fluctuating transverse dipole that drives the resonator and donates energy to it.

The distinction between perturbations that modify eigenstates and those that simply shift frequencies can also be clarified by considering Eq. (15), which gives the master equation in a reference frame where H_{spin} has not been eliminated. When a basis of spin-Hamiltonian eigenstates is used to express this equation, the coefficients $\mathcal{R}_{abcd}$ are determined by the relaxation superoperator Λ, and the coherent evolution associated with the commutator $-i[H_{\text{spin}}, \rho]$ causes coherences to oscillate at the Bohr frequencies of the system. Perturbations that affect the structure of spin-spin correlations in an eigenstate can modify both $\Lambda\rho$ and $-i[H_{\text{spin}}, \rho]$, while those that simply shift eigenfrequencies can only affect $-i[H_{\text{spin}}, \rho]$.

As examples of these two types of perturbations, we consider the way in which the spin-polarization process is modified by the presence of either the homonuclear dipolar Hamiltonian H_D or the chemical-shift Hamiltonian H_{CS}. These two Hamiltonians are [45]

$$H_D = \sum_{i<j} \omega_{ij}(3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j), \tag{45}$$

$$H_{\text{CS}} = \sum_i \omega_i I_{iz}, \tag{46}$$

where the secular dipolar couplings ω_{ij} in Eq. (45) are

$$\omega_{ij} = \frac{\mu_0 \gamma^2 \hbar}{8\pi r_{ij}^3}(1 - 3\cos^2\theta_{ij}), \tag{47}$$

and where ω_i in Eq. (46) represents the frequency offset of the ith spin due to the chemical shift. In Eq. (47), r_{ij} is the internuclear distance, θ_{ij} is the angle between the internuclear vector and the time-averaged magnetic field, and γ is the gyromagnetic ratio. Starting from a spin system in which $H_{\text{spin}} = 0$, we may compare the way in which spin relaxation is modified by "turning on" either of the Hamiltonians H_D, H_{CS}. If the dipolar coupling H_D is turned on when the spins are in a thermal state, spin-spin correlations quickly develop under the influence of H_D, and the spin-resonator interaction induces transitions between the correlated dipolar eigenstates. The magnitude of the transverse fluctuations $\langle I_x^2 + I_y^2 \rangle$ in these eigenstates plays a critical role in the relaxation of $\langle I_z \rangle$. If the chemical shift H_{CS} rather than H_D is turned on when the spins are in a thermal state, the spin Hamiltonian does not induce spin correlations since the spin eigenstates may be chosen as product states. In this case, any correlations which develop are due to the indirect spin-spin interaction discussed in Sec. IV. Correlated spin states appear in the product-state density matrix as off-diagonal terms, and these can only develop as a result of transfers from diagonal terms since the initial state was assumed to be thermal. If the oscillation frequencies of these off-diagonal terms are shifted sufficiently far from zero by H_{CS}, then the transfer from diagonal to off-diagonal terms will be averaged to zero, and $\langle I_z \rangle$ will relax exponentially to its thermal value, as shown in Sec. VI.

Averaging of the indirect spin-spin coupling by the chemical shift may be visualized using the semiclassical model. Consider an example where two semiclassical spins whose Larmor frequencies differ by $\delta\omega$ are initially aligned along the x axis, with $\delta\omega$ large compared to the nutation frequency of the spins due to the indirect coupling. The indirect torque exerted by spin 2 will initially tend to rotate spin 1 toward B_z, but after a time $t = \pi/\delta\omega$, the two spins will be aligned in opposite directions in the transverse plane, and the indirect torque on spin 1 will tend to rotate it away from B_z. The chemical-shift difference thus averages the indirect coupling to zero in this example. Indeed, the semiclassical model suggests that if frequency offsets of distinct spins are spaced sufficiently widely, all effects associated with the indirect coupling will be suppressed (i.e., $\langle I_z\rangle$ will decay exponentially with rate constant R_h). For spins 1/2, this conclusion is confirmed in Sec. VI.

In studying the way in which terms in the spin Hamiltonian modify the relaxation, we can gain insight by determining which spin transitions are associated with a given coefficient $\mathcal{R}_{abcd}$ of the relaxation superoperator. This is done by tracing the origin of the matrix elements A_1 and A_2 that contribute to $\mathcal{R}_{abcd}$ through products of the form $A_1A_2G_{mn}$. Each such product is derived from one of the terms in the expansion of the double commutator

$$i[i[\sigma,H_1(t_1)],H_1(t_2)] = -\sigma\, H_1(t_1)H_1(t_2) + H_1(t_1)\,\sigma\, H_1(t_2) + H_1(t_2)\,\sigma\, H_1(t_1) - H_1(t_2)H_1(t_1)\,\sigma, \tag{48}$$

where $H_1(t)$ is the interaction-frame Hamiltonian coupling the spins and the resonator, and where σ is the full density matrix that includes the reservoir degrees of freedom as well as those of the spins [31]. A term of the form $H_1(t_2)\sigma H_1(t_1)$, for example, has a bra making a transition at time t_1, and a ket making a transition at time t_2, while a term of form $H_1(t_2)H_1(t_1)\sigma$ has a bra make two transitions during the correlation time of the reservoir. Although all four terms on the right side of Eq. (48) are second order in H_1, the terms involving transitions in both a bra and a ket may be considered a product of two independent first-order transitions, while the remaining terms describe second-order processes that involve a transitory intermediate state. Note that the two factors of i appearing on the left side of Eq. (48) are associated with phase changes in transferred probability amplitude; for terms involving transitions in both a bra and a ket, these phase changes cancel, while for second-order transitions, the net effect is a sign change in the transferred probability amplitude. For reference later in the paper, we note that the coefficients $\mathcal{R}_{abcb}$, with $a \neq c$, depend on processes in which the sequence of transitions $|c\rangle \rightarrow |m\rangle \rightarrow |a\rangle$ occurs during the correlation time of the resonator, with $m \neq a,c$. The spins gain a quantum of energy during one of the transitions and lose a quantum during the other, and the matrix elements have the form

$$A_1A_2 = \langle a|I_u^\dagger|m\rangle\langle m|I_u|c\rangle. \tag{49}$$

In Eq. (49), as well as in the following two numbered equations, I_u can be either a raising operator or lowering operator. The coefficients $\mathcal{R}_{abcd}$, with $a \neq c$, $b \neq d$, involve transitions $|c\rangle \rightarrow |a\rangle$ and $\langle d| \rightarrow \langle b|$ and matrix elements of the form

$$A_1A_2 = \langle d|I_u^\dagger|b\rangle\langle a|I_u|c\rangle. \tag{50}$$

In particular, the coefficients $\mathcal{R}_{aacc}$, with $c \neq a$, involve the transitions $|c\rangle \rightarrow |a\rangle$ and $\langle c| \rightarrow \langle a|$ and matrix elements of the form

$$A_1A_2 = \langle c|I_u^\dagger|a\rangle\langle a|I_u|c\rangle. \tag{51}$$

$\mathcal{R}_{aacc}$ can be interpreted as the probability per unit time that a state from the continuum $\{|\mu,c\rangle\}$ makes the transition to the continuum $\{|\nu,a\rangle\}$, where a and c are fixed, while μ, ν range over the basis of reservoir states [31].

The selection rules implied by Eqs. (49) through (51) can be expressed in an alternative form using Eq. (16), which gives an explicit formula for the spin-relaxation superoperator Λ. The terms $I_+\rho I_-$ and $I_-\rho I_+$ appearing in Eq. (16) are associated with first-order transitions involving both a bra and a ket, while the terms $[I_-I_+,\rho]_+$ and $[I_+I_-,\rho]_+$ are associated with second-order transitions. Resonator-induced transfer from

$$|c\rangle\langle b| \rightarrow |a\rangle\langle b|,$$

with $a \neq c$, requires that either $I_-I_+|c\rangle$ or $I_+I_-|c\rangle$ include a contribution from $|a\rangle$, and this will be true precisely when a product of the form given by Eq. (49) is nonzero. Similarly, the transfer

$$|c\rangle\langle d| \rightarrow |a\rangle\langle b|,$$

with $a \neq c$, $b \neq d$, requires that $I_+|c\rangle\langle d|I_-$ or $I_-|c\rangle\langle d|I_+$ include a contribution from $|a\rangle\langle b|$, which is equivalent to the requirement that a product of the form given by Eq. (50) be nonzero.

VI. CHEMICAL-SHIFT HAMILTONIAN

A. Two spins

In analyzing the way in which $H_{\rm CS}$ modifies the spin-polarization process for a two-spin system, we use a basis set A composed of the following product states:

$$|1\rangle \equiv |++\rangle,$$
$$|2\rangle \equiv |+-\rangle,$$
$$|3\rangle \equiv |-+\rangle,$$
$$|4\rangle \equiv |--\rangle.$$

In the case where the internal spin Hamiltonian is zero or contains only chemical-shift interactions, A is a spin-energy eigenbasis, and since it is composed of product states, it can be used to develop an intuitive picture of the evolution of individual spins during the polarization process. We wish first to establish that if transfers between off-diagonal and diagonal terms are averaged to zero by $H_{\rm CS}$, then $\langle I_{1z}\rangle$ and $\langle I_{2z}\rangle$ will each relax exponentially to their thermal value with rate constant R_h, regardless of the initial state. Note that Eq. (51) implies that the rate constants $\mathcal{R}_{aacc}$ and $\mathcal{R}_{ccaa}$ for the transfer between populations ρ_{aa} and ρ_{cc} are nonzero only when $|a\rangle$ and $|c\rangle$ differ by a single spin flip. When these rate constants are nonzero, they have the same values as the rate constants governing population relaxation in the density matrix of a

single-spin system [i.e., the rate constants for a given spin to flip into or out of alignment with the field are $R_0(n_{\rm th}+1)$ and $R_0 n_{\rm th}$, respectively]. To see the implication for longitudinal relaxation, consider the evolution of

$$\langle I_{1z}\rangle = (\rho_{11}+\rho_{22}-\rho_{33}-\rho_{44})/2.$$

Transfers between populations ρ_{11} and ρ_{22} or between ρ_{33} and ρ_{44} do not change $\langle I_{1z}\rangle$ since these involve a flip of spin 2. If transfers between diagonal and off-diagonal terms are averaged to zero, then the only transfers which affect $\langle I_{1z}\rangle$ are those occurring between populations ρ_{11} and ρ_{33} or between ρ_{22} and ρ_{44}. Since the transfers within each of these pairs of populations are governed by the same rate constants that govern population transfer within a single-spin system, we find that spin 1 relaxes independently of spin 2 (i.e., its longitudinal relaxation is exponential regardless of the initial state).

If transfers between diagonal and off-diagonal matrix elements are not averaged to zero by $H_{\rm CS}$, then spin-spin correlations can have a dramatic effect on the polarization process. Consider an example where the resonator is at temperature $T_h = 0$ K, and the spins are initially in the state $c_2|2\rangle + c_3|3\rangle$, with $H_{\rm CS} = 0$. Either Eqs. (48) or (16) can be used to determine which spin transitions are induced by the resonator. Using the notation of Eq. (16), we find that the terms responsible for relaxation to the ground state population are associated with the transitions of both a bra and a ket to the ground state, and these terms have the form $I_+|i\rangle\langle j|I_-$, where i,j are both chosen from the set {2,3}. Equation (16) implies that during a time interval Δt that is short compared to spin-relaxation times, resonator-induced transitions from $c_2|2\rangle$ and $c_3|3\rangle$ transfer probability amplitudes $c_2\delta$ and $c_3\delta$ to the ground-state ket, respectively, and that similar transfers of probability amplitudes occur between the bras. (Here δ is given by $R_0\,\Delta t$.) These transitions cause the ground-state population to increase by

$$\begin{aligned}&(c_2\delta + c_3\delta)\,|1\rangle\langle 1|\,(c_2^*\delta^* + c_3^*\delta^*)\\ &\quad = |\delta|^2(|c_2|^2 + |c_3|^2 + c_2c_3^* + c_3c_2^*)|1\rangle\langle 1|. \qquad (52)\end{aligned}$$

The change in the ground-state population depends on the relative phases of the coefficients c_2 and c_3. If $c_2 = -c_3$, for example, then the net change in the ground-state population is zero. The spins cannot decay by spontaneous emission because the probability amplitudes transferred from states 2 and 3 to the ground state sum to zero. (Note that this result can also be obtained from symmetry arguments: the singlet state is isolated from the manifold of triplet states since the relaxation conserves angular momentum.) In a statistical ensemble where the phases of c_2 and c_3 are randomly distributed, the ensemble average of the term $c_2c_3^* + c_3c_2^*$ will be zero, and states 2 and 3 may be considered to relax independently to the ground state (i.e., each of the two spins relaxes independently of the other). If $c_2 = c_3$, decay to the ground state is twice as fast as for the uncorrelated product states 2 and 3. Finally, note that if the eigenfrequencies of these two states differ sufficiently due to a chemical shift difference, then $c_2c_3^*$ and $c_3c_2^*$ will oscillate quickly on the time scale of the spin relaxation and the contribution associated with these terms will be averaged to zero, causing the two spins to relax independently.

On the right side of Eq. (52), the respective contributions $|\delta|^2|c_2|^2$ and $|\delta|^2|c_3|^2$ are associated with the master-equation coefficients $\mathcal{R}_{1122}$ and $\mathcal{R}_{1133}$ that govern the transfer from the populations of states 2 and 3 to the ground-state population. The remaining contributions $|\delta|^2c_2c_3^*$ and $|\delta|^2c_3c_2^*$ are associated with the coefficients $\mathcal{R}_{1123}$ and $\mathcal{R}_{1132}$, which govern the transfer from the off-diagonal elements ρ_{23} and ρ_{32} to the ground-state population. Within the formalism of the master equation in the product-state basis, these transfers are responsible for increasing the spontaneous emission rate or decreasing it to zero due to the presence of spin-spin correlations.

If the spins relax from a completely disordered state while coupled to a resonator at 0 K, the resonator induces a negative correlation between states 2 and 3 by second-order transitions such as $|2\rangle \to |1\rangle \to |3\rangle$ and $|3\rangle \to |1\rangle \to |2\rangle$, which introduce a sign change into the transferred probability amplitude. These transitions cause the development of spin-spin correlations that slow the rate of spontaneous emission (i.e., the development of singlet spin order). In the master-equation formalism, these transitions appear as transfers from the populations of states 2 and 3 to zero-quantum operators with matrix elements between states $|2\rangle$ and $|3\rangle$. The transfers will be averaged to zero by $H_{\rm CS}$ if the chemical shift difference $\Delta\omega$ is sufficiently large that the laboratory-frame zero-quantum operators oscillate quickly on the time scale of the transfers. More generally, the condition for $H_{\rm CS}$ to efficiently suppress the development of resonator-induced correlations in a two-spin thermal system is

$$\Delta\omega/2\pi \gg R_0(n_{\rm th}+1),$$

since the rate constants $\mathcal{R}_{23ii}$, $\mathcal{R}_{32ii}$ for the transfer from populations to zero-quantum operators have magnitudes $\leqslant R_0(n_{\rm th}+1)$.

B. *N* spins

Certain results of the previous section can be generalized to a system of N spins. In particular, Appendix D shows that if the resonator-induced transfer between product-state populations and certain zero-quantum operators is suppressed, then $\langle I_z\rangle$ relaxes exponentially to thermal equilibrium with rate constant R_h, regardless of the initial state. This result can be interpreted to mean that individual spins emit and absorb independently from uncorrelated product states. In the case where the system is initially in a thermal state, the matrix elements of the interaction Hamiltonian allow for two types of resonant processes that produce terms off-diagonal in the product states. Associated with these resonant processes are two types of terms in Eq. (16). Terms of the form $I_-|a\rangle\langle a|I_+$ or $I_+|a\rangle\langle a|I_-$ can generate the operator $|b\rangle\langle c|$ by means of the two transitions $|a\rangle \to |b\rangle$ and $\langle a| \to \langle c|$. These transitions can induce zero-quantum operators with matrix elements between states that differ by two spin flips. (In a four-spin system, for example, the resonator can induce a zero-quantum term between $|b\rangle = |++--\rangle$ and any of the states $|-++-\rangle$, $|-+-+\rangle$, $|+--+\rangle$, or $|+--+\rangle$ since each of these states can be obtained from $|b\rangle$ by flipping two spins in opposite directions.) The same operators are generated by terms in Eq. (16) that have the form $[I_-I_+,|a\rangle\langle a|]_+$ or $[I_+I_-,|a\rangle\langle a|]_+$,

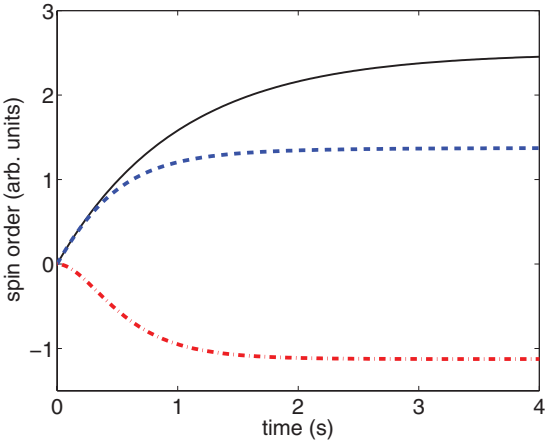

FIG. 3. (Color online) Simulated relaxation of five isochronous spins that interact only with the resonator and are initially completely disordered. The dashed (blue) and dash-dotted (red) curves show the respective evolution of $\langle I_z \rangle$ and $\langle I_x^2 + I_y^2 - 5/2 \rangle$. The solid curve shows ideal exponential relaxation with rate constant $R_0 = 1\ \mathrm{s}^{-1}$ toward full polarization, for purposes of comparison with $\langle I_z \rangle$. As in all simulations presented in this paper, the resonator temperature is $T_h = 0$ K.

and these involve a second-order transition such as $|a\rangle \rightarrow |m\rangle \rightarrow |b\rangle$.

If these zero-quantum operators oscillate sufficiently slowly, trapping or accelerated longitudinal relaxation can occur, depending on whether the superposition is associated with constructive or destructive interference between the transferred probability amplitudes. If the frequencies are sufficiently large, however, then all transfers between product-state populations and off-diagonal terms of the density matrix will be averaged to zero by H_{CS}, and the spins will relax independently.

Figures 3 through 6 illustrate the way in which the longitudinal relaxation of a five-spin system is affected by small chemical-shift differences. In Figs. 3 and 4, the initial spin state is completely disordered, while in Figs. 5 and 6, the

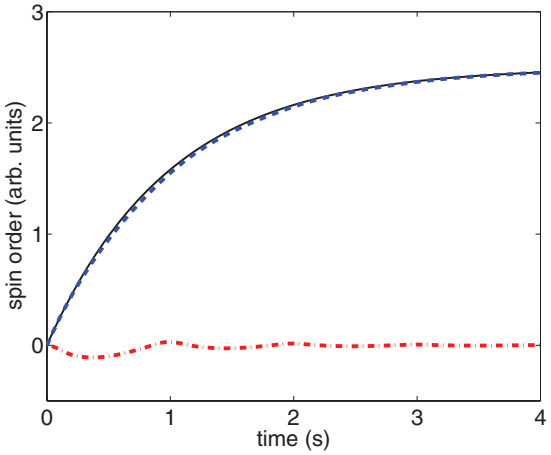

FIG. 4. (Color online) Adding chemical shift offsets to the simulation of Fig. 3, such that the Larmor frequencies of the five spins are spaced in steps of 1 Hz, causes the indirect spin-spin torques to be modulated quickly enough that their contribution to relaxation is suppressed.

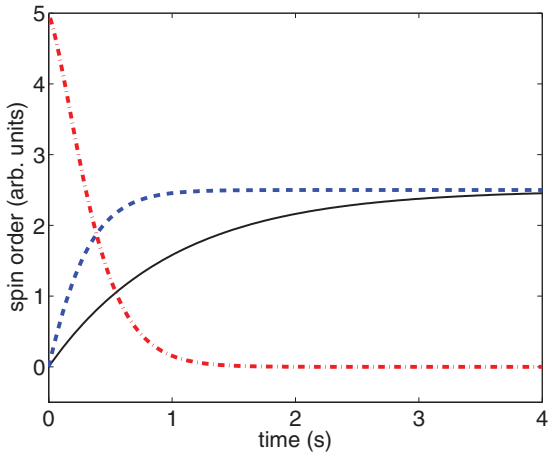

FIG. 5. (Color online) Simulated relaxation of five isochronous spins that interact only with the resonator and are initially aligned along the x axis. The dashed (blue) and dash-dotted (red) curves show the respective evolution of $\langle I_z \rangle$ and $\langle I_x^2 + I_y^2 - 5/2 \rangle$. The solid curve shows ideal exponential relaxation with rate constant $R_0 = 1\ \mathrm{s}^{-1}$ toward full polarization, for purposes of comparison with $\langle I_z \rangle$.

initial state has the spins aligned along the x axis. The dashed and dash-dotted curves show the simulated relaxation of $\langle I_z \rangle$ and $\langle I_x^2 + I_y^2 - 5/2 \rangle$, respectively. [Recall from the discussion of Eq. (38) that the contribution of spin-spin correlations to $d\langle I_z \rangle/dt$ is in general given by $R_0 \langle I_x^2 + I_y^2 - N/2 \rangle$.] The solid curve shows the ideal exponential relaxation with rate constant $R_0 = 1\ \mathrm{s}^{-1}$ toward full polarization, for purposes of comparison with $\langle I_z \rangle$. In Figs. 3 and 5, $H_{\mathrm{CS}} = 0$, while in Figs. 4 and 6, each of the spins has a different chemical shift, and the five chemical shifts are spaced in steps of 1 Hz. For the initially disordered system, this spacing of chemical shifts is sufficient to suppress the contribution of spin-spin correlations to longitudinal relaxation. The value

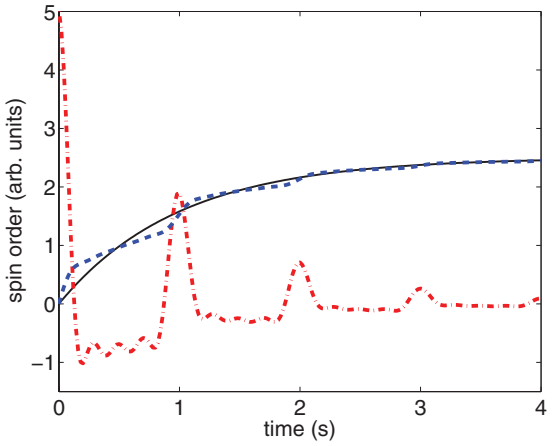

FIG. 6. (Color online) Adding chemical shift offsets to the simulation of Fig. 5, with the Larmor frequencies of the five spins spaced in steps of 1 Hz, causes the indirect spin-spin torques to be modulated. When the transverse spin components are initially aligned, the indirect torques add coherently, and so a faster modulation would be needed to completely suppress their effect on longitudinal relaxation.

of $\langle I_x^2 + I_y^2 - 5/2\rangle$ oscillates without ever developing a large-enough magnitude to affect the relaxation substantially. This oscillation is consistent with the conclusion in Sec. V that a chemical-shift difference between two spins modulates the sign of the indirect spin-spin torque that couples them; in Fig. 4, this modulation of the indirect torques appears as an oscillation in the contribution of spin-spin correlations to $d\langle I_z\rangle/dt$. Alternatively, we can say that in a product-state eigenbasis, resonator-induced correlations must appear as zero-quantum operators; these operators oscillate due to the presence of $H_{\rm CS}$, and transfers from populations to oscillating operators are averaged to zero. Consistent with the discussion of Eqs. (41) and (42), we see that when the transverse spins are initially aligned, the indirect torques affect the relaxation much more strongly than when the spins are initially disordered since the torques add constructively in the aligned system. The effect of these torques can be seen in the oscillations of $\langle I_z\rangle$ about the solid curve corresponding to exponential decay. As might be expected, these oscillations are correlated with sign changes in $\langle I_x^2 + I_y^2 - 5/2\rangle$.

VII. DIPOLAR HAMILTONIAN PLUS CHEMICAL-SHIFT HAMILTONIAN

A. Angular momentum conservation in two-spin and three-spin systems

We turn our attention to systems of spins 1/2 that evolve under the secular dipolar Hamiltonian H_D and the chemical-shift Hamiltonian $H_{\rm CS}$, beginning with two-spin and three-spin systems which are in a limiting regime where one of these terms is much larger than the other. If the Hamiltonian is purely dipolar, then the energy eigenstates are also angular-momentum eigenstates:

$$\begin{aligned} |1,1\rangle &\equiv |++\rangle, \\ |1,0\rangle &\equiv (|+-\rangle + |-+\rangle)/\sqrt{2}, \\ |1,-1\rangle &\equiv |--\rangle, \\ |0,0\rangle &\equiv (|+-\rangle - |-+\rangle)/\sqrt{2}. \end{aligned}$$

Here state $|I,M\rangle$ has angular momentum I and z component M. When this basis set is used to express the spin-relaxation superoperator Λ of Eq. (16), there is no coupling between the populations and off-diagonal terms; longitudinal relaxation depends only on the transfers between populations. Resonator-induced relaxation cannot transfer population between angular momentum manifolds since $H_{\rm spin}$ does not break the symmetry of angular-momentum conservation. If the resonator is at temperature $T_h = 0$ K, the initial population of the $I = 1$ manifold will relax to the ground state $|1,1\rangle$, while the initial population of the $I = 0$ state will be "trapped" away from the ground state. Note that similar considerations are used in Sec. IV to show that conservation of angular momentum causes trapping in systems of noninteracting, isochronous spins.

A chemical-shift difference $\Delta\omega$ that is small compared to the noncommuting terms of the dipolar Hamiltonian cannot significantly affect longitudinal relaxation since a weak perturbation to the Hamiltonian does not change the rate constants $\mathcal{R}_{aabb}$ for transfer between populations. In the regime where $H_D \gg H_{\rm CS}$, the dipolar Hamiltonian controls the structure of the spin-spin correlations associated with the energy eigenstates, and these correlations determine the strength of the transverse spin fluctuations that contribute to spontaneous emission from the eigenstates.

If $H_D \ll H_{\rm CS}$, then the energy eigenstates are weakly perturbed from product states, and the longitudinal relaxation will proceed exponentially with rate constant R_h, provided the zero-quantum frequency is sufficiently large to disrupt the development of resonator-induced spin-spin correlations. This result generalizes to larger systems: if the chemical shift differences are large enough to ensure that the energy eigenstates are weakly perturbed from product states, then the magnitudes of the zero-quantum frequencies will determine whether the spins relax to thermal equilibrium.

For a collection of three spins 1/2, the rules for the addition of angular momentum allow the system to be represented as as a single angular momentum $I = 3/2$ and two angular momenta $I = 1/2$. For our purposes, it is convenient to define one of the $I = 1/2$ angular momenta to be

$$\begin{aligned} |1/2,+1/2\rangle &= (1/C)[(\omega_{13}-\omega_{23})|++-\rangle + (\omega_{23}-\omega_{12})|+-+\rangle + (\omega_{12}-\omega_{13})|-++\rangle], \\ |1/2,-1/2\rangle &= (1/C)[(\omega_{23}-\omega_{13})|--+\rangle + (\omega_{12}-\omega_{23})|+--\rangle + (\omega_{13}-\omega_{12})|+--\rangle], \\ C &\equiv (\omega_{12}-\omega_{13})^2 + (\omega_{12}-\omega_{23})^2 + (\omega_{13}-\omega_{23})^2, \end{aligned}$$

where the secular dipolar couplings ω_{ij} are defined by Eq. (47). The states of this angular momentum manifold are also eigenstates of H_D:

$$H_D|1/2,+1/2\rangle = H_D|1/2,-1/2\rangle = 0.$$

If $H_{\rm CS} = 0$, then the population which begins in this manifold can move only within the manifold during resonator-induced cooling. For an initially disordered system cooled by a resonator at temperature $T_h = 0$ K, one-fourth of the population will eventually be trapped in the nondecaying state $|1/2,+1/2\rangle$. As in the case of two spins, additional terms in the spin Hamiltonian can only be effective in suppressing this spin trapping if they significantly perturb the spin eigenstates. Since $H_{\rm CS}$ does not conserve angular momentum, chemical shifts of magnitude comparable to the dipolar coupling will in general break the selection rule responsible for trapping the population away from the ground state. A chemical shift Hamiltonian $H_{\rm CS} \ll H_D$ cannot affect this trapping process, however, since the relaxation superoperator Λ does not couple

the population of $|1/2, +1/2\rangle$ to any off-diagonal term of the density matrix.

B. Symmetry breaking by $H_D + H_{CS}$

Simulations of resonator-induced cooling in systems containing a few spins suggest that as the number of spins is increased, the Hamiltonian $H_D + H_{CS}$ becomes increasingly effective in coupling manifolds of different angular momentum and thereby facilitating relaxation to thermal equilibrium. Thirty structures containing carbon, nitrogen, oxygen, and either 3, 4, or 5 hydrogen atoms were randomly selected from the Cambridge Structural Database (CSD) [46], and the Hamiltonian H_D that governs dipolar interactions between H nuclei was calculated for each of the selected structures, using the coordinates provided in the database. For each structure, two simulations of resonator-induced cooling were performed; one of these used H_D as the spin Hamiltonian, while the other used $H_D + H_{CS}$. Rather than trying to estimate the anisotropic chemical shifts for the H nuclei in each of these structures, we assigned chemical shifts randomly within a range of 0–10 ppm to roughly characterize the way in which the presence of H_{CS} can affect the relaxation in systems of a few dipole-dipole coupled spins. Specifically, the respective chemical-shift Hamiltonians for the three-spin, four-spin, and five-spin systems were

$$H_{CS,3} = (\omega_0 \times 10^{-6})(8.1\, I_{1z} + 9.1\, I_{2z} + 1.3\, I_{3z}),$$
$$H_{CS,4} = (\omega_0 \times 10^{-6})\,(9.1\, I_{1z} + 6.3\, I_{2z} + 1.0\, I_{3z} + 2.8\, I_{4z}),$$
$$H_{CS,5} = (\omega_0 \times 10^{-6})(9.6\, I_{1z} + 4.9\, I_{2z} + 8.0\, I_{3z} + 1.4\, I_{4z} + 4.2\, I_{5z}),$$

where $\omega_0/2\pi = 600$ MHz, and where the spins were numbered according to the order in which they are listed in the database entry for the structure. For all simulations, the initial spin state was completely disordered. The number of quanta in the resonator was set to zero to simulate the limiting case where the temperature approaches 0 K, and the rate constant R_0 for spontaneous emission was set to 1.0 s^{-1}. (See the supplementary information for a full set of relaxation plots [47].)

In Figs. 7 through 11, the dash-dotted curves show relaxation occurring in the presence of the dipolar Hamiltonian H_D, while the dashed curves show relaxation in the presence of $H_D + H_{CS}$. For each simulation, the upper curve shows the relaxation of $\langle I_z\rangle$, and the lower shows $\langle I_x^2 + I_y^2 - N/2\rangle$, which can be interpreted as the contribution of spin-spin correlations to $d\langle I_z\rangle/dt$. Each figure includes a solid curve showing the ideal exponential relaxation with rate constant R_0 toward full polarization, for purposes of comparison with $\langle I_z\rangle$.

For the three-spin systems governed by H_D, the relaxation plots were all similar: the systems relaxed to the trapped state on a similar time scale. The dash-dotted curves of Fig. 7 show one of these three-spin simulations. $\langle I_z\rangle$ relaxes to a steady-state value of 5/4, rather than to 3/2, the value that would correspond to full polarization. This is consistent with the prediction that 25% of the initial population remains trapped in an $I = 1/2$ manifold, rather than relaxing to the ground state.

A variety of polarization curves were observed in the four-spin and five-spin systems governed by H_D. The dash-dotted curves of Figs. 8 and 9 illustrate the range of results obtained

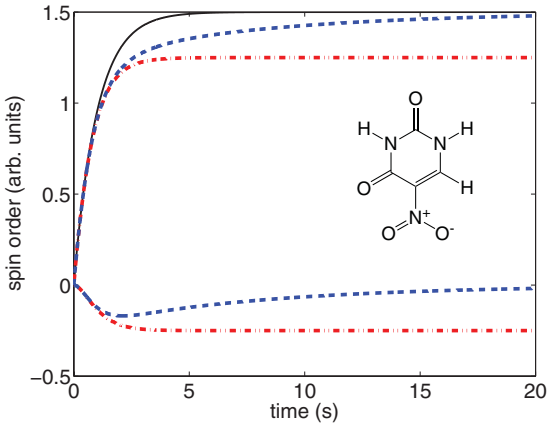

FIG. 7. (Color online) Cooling of a system of three H nuclei (CSD entry: nimfoe) from an initially disordered state. The dash-dotted curves (red) show relaxation under the dipolar Hamiltonian H_D, while the dashed curves (blue) show relaxation under $H_D + H_{CS}$. For each simulation, the upper curve shows the relaxation of $\langle I_z\rangle$, and the lower shows $\langle I_x^2 + I_y^2 - 3/2\rangle$. The solid curve shows ideal exponential relaxation with rate constant $R_0 = 1\ s^{-1}$ toward full polarization, for purposes of comparison with $\langle I_z\rangle$.

for four-spin systems, while Figs. 10 and 11 illustrate the five-spin results. In each case, an initial period of fast polarization is followed by a period in which relaxation is slow or absent. For the structure of Fig. 8, a simulation of 100 s of relaxation yields

$$\langle I_z\rangle = \langle I_x^2 + I_y^2\rangle = 1.8750, \tag{53}$$

which corresponds to a trapped state since the derivative

$$\frac{d}{dt}\langle I_z\rangle = R_0\big(\langle I_x^2 + I_y^2\rangle - \langle I_z\rangle\big)$$

is zero under these conditions. Note that Eq. (53) can be rationalized by assuming that population is trapped in a single

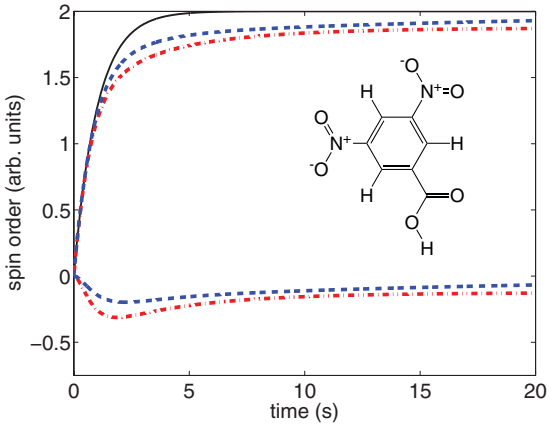

FIG. 8. (Color online) Cooling of a system of four H nuclei (CSD entry: cukcam04) from an initially disordered state. The dash-dotted curves (red) show relaxation under the dipolar Hamiltonian H_D, while the dashed curves (blue) show relaxation under $H_D + H_{CS}$. For each simulation, the upper curve shows the relaxation of $\langle I_z\rangle$, and the lower shows $\langle I_x^2 + I_y^2 - 4/2\rangle$. The solid curve shows ideal exponential relaxation with rate constant $R_0 = 1\ s^{-1}$ toward full polarization, for purposes of comparison with $\langle I_z\rangle$.

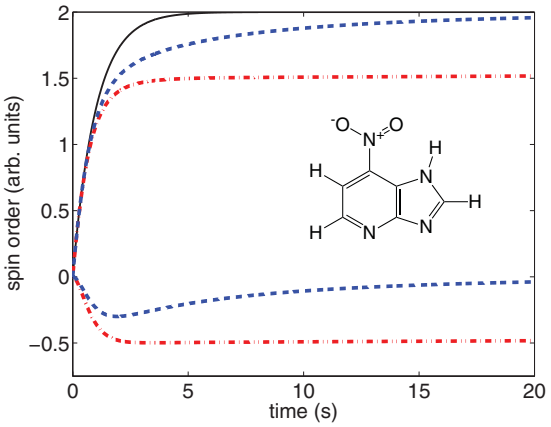

FIG. 9. (Color online) Cooling of a system of four H nuclei (CSD entry: vazmep) from an initially disordered state. The curves are defined in the same way as in Fig. 8.

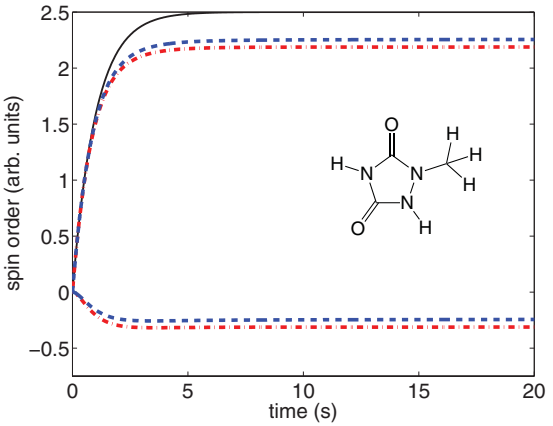

FIG. 11. (Color online) Cooling of a system of five H nuclei (CSD entry: wijzoe) from an initially disordered state. The curves are defined in the same way as in Fig. 10.

$I = 0$ manifold. Both the initial state and the final state have $1/16$ of the population in this manifold; the rest of the population relaxes to the ground state of the $I = 2$ manifold. Three of the ten four-spin systems that were simulated relaxed to the same level, while one of the systems relaxed to a level that can be rationalized by assuming that $3/16$ of the population is trapped in an $I = 1$ manifold. After 100 s of simulated evolution, none of the five-spin systems showed evidence of having relaxed to a trapped state (i.e., a state from which the emission is essentially zero during tens of seconds).

Although the dash-dotted curves of Fig. 9 appear extremely flat after $t \approx 5$ s, they correspond to slow relaxation rather than to a trapped state. After 100 s of relaxation, $\langle I_z \rangle$ and $\langle I_x^2 + I_y^2 \rangle$ have not yet relaxed to the same value, and the value $\langle I_z \rangle \approx 1.58$ at the end of this period cannot be rationalized by assuming that the population of certain angular-momentum

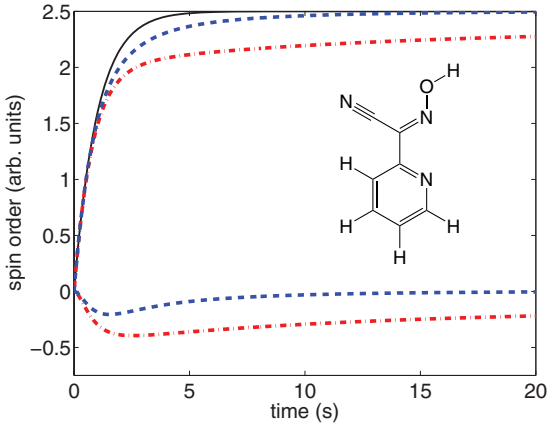

FIG. 10. (Color online) Cooling of a system of five H nuclei (CSD entry: cejmaf) from an initially disordered state. The dash-dotted curves (red) show relaxation under the dipolar Hamiltonian H_D, while the dashed curves (blue) show relaxation under $H_D + H_{CS}$. For each simulation, the upper curve shows the relaxation of $\langle I_z \rangle$, and the lower shows $\langle I_x^2 + I_y^2 - 5/2 \rangle$. The solid curve shows ideal exponential relaxation with rate constant $R_0 = 1\ \mathrm{s}^{-1}$ toward full polarization, for purposes of comparison with $\langle I_z \rangle$.

manifolds is trapped since this value is not a multiple of $1/16$. Note as well that between the times $t = 20$ s and $t = 100$ s, $\langle I_z \rangle$ relaxes from 1.52 to 1.58: slow spontaneous emission continues during this period. A similar slow relaxation was observed in several of the four-spin and five-spin systems evolving under H_D.

In most cases, the addition of H_{CS} to the simulations increased the spontaneous emission rate during the period in which $\langle I_z \rangle$ is slowly relaxing or trapped; in particular, none of the systems evolving under $H_D + H_{CS}$ showed evidence of being in a trapped state after 100 s of relaxation, although several showed slow relaxation that had $\langle I_z \rangle$ decrease by only a few percent between $t = 20$ s and $t = 100$ s. The effect of H_{CS} on weakly emitting correlated states can be seen by examining the evolution of $\langle I_x^2 + I_y^2 - N/2 \rangle$ in Figs. 7 through 11, shown in the curves that drop below zero. In contrast with the plots in Figs. 4 and 6, the disruption of spin-spin correlations by the chemical-shift Hamiltonian does not here correspond to oscillations in $\langle I_x^2 + I_y^2 - N/2 \rangle$; rather it corresponds to the relaxation of $\langle I_x^2 + I_y^2 - N/2 \rangle$ toward zero. This can be rationalized by first recalling that in Figs. 4 and 6, the energy eigenstates are uncorrelated product states, and spontaneous emission from these states can be interpreted as independent emission by individual spins. The transfer of populations between such states does not affect $\langle I_x^2 + I_y^2 - N/2 \rangle$; spin-spin correlations that weaken spontaneous emission appear as slowly oscillating zero-quantum coherences that develop due to resonator-induced coupling between populations and these coherences. For systems governed by H_D or $H_D + H_{CS}$, however, the energy eigenstates involve correlated motions of the spins, and the transfer of population into weakly emitting eigenstates appears as gradual drop in $\langle I_x^2 + I_y^2 - N/2 \rangle$. It is natural to rationalize Figs. 7 through 10 by concluding that the chemical-shift Hamiltonian facilitates the process of "siphoning off" the population from such weakly emitting states; that is, in these simulations, the presence of H_{CS} tends to increase the emission rates of such states, thereby enabling transitions to more strongly emitting states that can quickly relax to the ground state. The lack of oscillations in $\langle I_x^2 + I_y^2 - N/2 \rangle$ is consistent with the reasonable guess that the spin-resonator interaction

cannot create slowly oscillating coherences in these systems. Due to the magnitude and nondegeneracy of the dipolar couplings and chemical shifts in these simulations, zero-quantum frequencies of a few Hz or less are not expected, as would be required for resonator-induced development of oscillating coherences.

VIII. SPIN POLARIZATION IN A FIELD GRADIENT OR IN A WARM SAMPLE

A. Magnetic-resonance force microscope

A torsional resonator prototype designed for force-detected NMR spectroscopy has been used so far to illustrate the theoretical results, but the analysis can easily be adapted to other resonator geometries and experimental conditions. As an example, we consider the problem of cooling spins with a magnetic-resonance force microscope. MRFM depends on the presence of a strong field gradient, which causes the Larmor frequency to vary sharply with spatial position in the sample. A "sensitive slice" of resonant spins interacts with the mechanical oscillator, and the sample is imaged by shifting the position of this sensitive slice. Since the signal strength is proportional to the gradient, the experimental setup is designed to yield the largest possible gradient.

The analysis in Secs. IV through VII began from a limiting case in which all spins experience the same field. We note first that an ideal MRFM experiment may be considered the opposite limiting case since the gradient would ideally be strong enough to select a resonant slice containing only a single spin. "Turning on" the homonuclear dipolar coupling in these two limiting cases modifies the relaxation in distinct ways. Perturbing a system of multiple isochronous spins by H_D breaks the symmetry of angular-momentum conservation and prevents the trapping of the population. If only a single resonant spin is efficiently polarized, the effect of a strong dipolar-coupling network is to spread the polarization throughout the network, thereby diminishing the polarization of the detected spin. More generally, resonator-induced cooling of a spin sample in an MRFM experimental setup will depend on spin diffusion (i.e., on equilibration of magnetization within the sample due to spin-spin dipolar interactions).

From Eq. (45), the homonuclear dipolar interaction between spins i and j is governed by the operator

$$3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j = 2I_{iz}I_{jz} - \tfrac{1}{2}(I_{i+}I_{j-} + I_{i-}I_{j+}). \quad (54)$$

It is the "flip-flop" transitions governed by $(I_{i+}I_{j-} + I_{i-}I_{j+})$ that are responsible for the transfer of polarization between spins. If the difference $\Delta\omega_0$ between the Larmor frequencies of spins i and j is large compared to the secular dipolar coupling ω_{ij}, these flip-flop transitions will be averaged to zero, and spin diffusion will be suppressed. For samples containing multiple spins and large field gradients, the contribution of spin diffusion to resonator-induced cooling depends on the relative strengths of the gradients, the homonuclear dipolar couplings, and any additional spin interactions that cause significant frequency shifts.

In the case where the sensitive slice contains only a single spin, and where the gradient is large enough to suppress spin diffusion, the spin relaxes exponentially toward thermal equilibrium with the resonator. The relaxation is governed by Eq. (20):

$$\frac{d}{dt}\langle I_z - \langle I_z\rangle_{\rm th}\rangle = -R_h\langle I_z - \langle I_z\rangle_{\rm th}\rangle.$$

For a given resonator geometry, an explicit expression for the rate constant R_h can be obtained from arguments similar to those used in deriving Eqs. (11) and (21). Letting u denote the resonator coordinate and $\mathbf{B}(u)$ the field at the spin, we consider as an example a translational mechanical resonator for which $d\mathbf{B}/du$ is transverse to the time-averaged field $\mathbf{B}_0$. Choosing the x axis to be parallel to $d\mathbf{B}/du$ and the z axis to be parallel to $\mathbf{B}_0$ gives the following first-order approximation to $\mathbf{B}(u)$:

$$B_x(u) \approx \frac{dB_x}{du}u, \quad (55a)$$

$$B_y(u) \approx 0, \quad (55b)$$

$$B_z(u) \approx B_0. \quad (55c)$$

Note that Eqs. (55a) and (55c) are formally identical to Eqs. (3a) and (3b), while Eq. (55b) is similar to Eq. (2b). The first-order Hamiltonian has the same form as Eq. (11), and the coupling constant g is given by

$$g = \frac{-\gamma}{2}\sqrt{\frac{\hbar}{2m_h\omega_h}}\frac{dB_x}{du}, \quad (56)$$

where m_h is the mass of the resonator. Equation (56) can be obtained from Eq. (9) by substituting m_h for the moment of inertia I_h, and by substituting the linear derivative dB_x/du for the angular derivative $dB_x/d\theta$. From Eq. (21), the formula for R_h is

$$R_h = 2g^2\tau_h(2n_{\rm th}+1).$$

The magnetic-resonance force microscopes used so far have mechanical frequencies that are orders of magnitude smaller than the Larmor frequency. Since the resonance condition $|\omega_h| = |\omega_0|$ is required for the energy-conserving exchange of quanta between the spins and the resonator, the efficient spin-polarization process analyzed in this paper cannot occur with these low-frequency oscillators. A closely related process has been observed, however, in an experiment where an MRFM cantilever induced relaxation during adiabatic sweeps of an applied rf field [48]. For simplicity, we consider the relaxation occurring during a period when the rf field is resonant with the Larmor frequency. The rotating-frame description of the spin system has a static field B_1 in the transverse plane, and field fluctuations along the z axis that are resonant with nutation about B_1 can cause spin flips with respect to a quantization axis parallel to B_1 [48]. In the case where a mode of the MRFM cantilever has significant spectral density at the

nutation frequency, and where the motion of the mode causes variation in B_z, thermal equilibration between the mode and the rotating-frame spin system will result in spin relaxation which can be analyzed using the theoretical framework developed in this paper. Note that these experimental conditions correspond to the limiting case of a high-temperature resonator; at a proton nutation frequency of 100 kHz, for example, the temperature of the mechanical mode would have to be at most a few μK to induce a polarization of order unity along B_1.

B. Warm sample with an externally cooled mode

Given the success of resolved-sideband cooling [23] and feedback cooling [24] in cooling mechanical oscillators below the temperature of the thermal bath, it is appealing to consider the possibility of using a cold mechanical mode to polarize spins in a "warm" sample (i.e., a sample where the translational degrees of freedom are at a significantly higher temperature than the mechanical resonator). As a heuristic example, we consider a spin sample that is simultaneously heated by the lattice and cooled by the resonator. Let P_l and P_h denote the thermal polarization at the lattice temperature and the resonator temperature, respectively. If spin-lattice relaxation and resonator-induced relaxation are both exponential and have the respective rate constants R_1 and R_h, the steady-state spin polarization is

$$P_\infty = \frac{R_1 P_l + R_h P_h}{R_1 + R_h},$$

and the rate constant for relaxation toward P_∞ is $R_1 + R_h$. In the limiting case where the lattice temperature is sufficiently high that $P_l \ll P_h$, and where $R_1 \lesssim R_h$, we have

$$P_\infty \sim \frac{R_h}{R_1 + R_h} P_h.$$

For example, with $P_h \sim 1$, the rate constants $R_1 \sim R_h \sim 1\ \mathrm{s}^{-1}$ would give $P_\infty \sim 0.5$ and a longitudinal relaxation time of $\sim$0.5 s.

In addition to the technical difficulties associated with the experimental realization of this polarization scheme, a more fundamental limitation should be noted. Resolved-sideband cooling and feedback cooling damp the mechanical motion, and the damping of the resonator limits its ability to polarize spins. An effective scheme for polarizing warm samples with a cold resonator requires a cooling process that leaves the resonator responsive to driving by spin fluctuations (i.e., a cooling process that does not heavily damp the resonator). Formally, the rate constant R_h is proportional to the mechanical ring-down time τ_h, which limits the buildup of the spin-resonator correlations responsible for energy transfer. The applicability of a mechanical cooling process to nuclear-spin polarization depends on both the temperature drop in the mechanical mode and the change in τ_h.

More generally, the modification of the resonator's properties by an external cooling process can affect its usefulness for experiments involving the polarization and/or detection of a warm spin sample. As an example, consider the scheme of using hyperpolarized spins to cool a mechanical mode, which might in turn be used to polarize a warm spin sample of interest and detect its NMR spectrum [21]. A detailed analysis has been performed for a system that consists of a stream of hyperpolarized xenon atoms interacting with a warm torsional resonator [49]. The relaxation of the spin-resonator system toward thermal equilibrium cools the resonator, and the flow of xenon past the resonator replenishes the supply of cold spins. In the regime where the interaction between the spins and the resonator is sufficiently weak that one of the modes of the system can be identified as a perturbed mechanical mode, the temperature of the resonator drops by less than 20% due to the interaction with the cold spins. Increasing the magnitude of g, the spin-resonator coupling constant, or $\langle I_z \rangle$, the summed z component of the xenon spins, gives a more strongly coupled system and thus more efficient cooling. However, in the regime where the resonator temperature is approximately 4/5 the temperature of the warm thermal bath, a transition in the nature of the spin-resonator system occurs, and the modes of the system cannot be identified as perturbed mechanical or spin modes; rather, the modes involve highly correlated motions of the spins and the resonator. In the strongly coupled regime, fluctuations in the correlation between the transverse spin and resonator coordinate are quickly converted to large mechanical fluctuations, and as a result, the mechanical fluctuations are not decreased by the presence of the cold spins. Expressing the mechanical fluctuations in terms of a noisy thermal torque acting on the resonator shows that cooling due to strong interactions with hyperpolarized spins does not improve the resonator's sensitivity as a detector of an applied torque (e.g., as a detector of the NMR spectrum of a warm spin sample).

IX. SIMULATION METHODS

For all simulations presented in this paper, the rate constant for spontaneous emission by the spins into the resonant mode is $R_0 = 1\ \mathrm{s}^{-1}$, the Larmor frequency is 600 MHz, and the resonator temperature is $T_h = 0$ K. This value of R_0 is similar to that calculated for the resonator of Ref. [21], which has a frequency $\omega_h/2\pi \approx 600$ MHz. At this frequency, the mK temperatures achievable in a dilution refrigerator yield a spin polarization of $P \sim 1$, with $n_{\mathrm{th}} \ll 1$, and so the relaxation is occurring in the low-temperature limit. For systems including up to five spins, the relaxation governed by the reduced master equation (15) was simulated using the GAMMA library [50], while for larger systems, formulas for the spontaneous emission rate of states $|I,M\rangle$ [22] were used to simulate resonator-induced cooling within angular-momentum manifolds. The simulations of the relaxation of $\langle I_z \rangle$ and $\langle I_x^2 + I_y^2 - N/2 \rangle$ correspond to laboratory-frame evolution.

X. CONCLUSION

This paper has provided a theoretical framework for the study of resonator-induced polarization of nuclear spins. The Hamiltonian

$$H_1 = g(I_+ a^\dagger + I_- a),$$

obtained by approximating the field to first order in the resonator coordinate, was shown to be sufficient for the study of resonator-induced relaxation since the corrections to the master equation obtained by approximating the field to higher order are negligible. In the regime where the bandwidth of the resonator's fluctuations is broad compared to the width of the NMR spectrum, the equation of motion for $\langle I_z \rangle$ is

$$\frac{d}{dt}\langle I_z \rangle = -R_h \langle I_z \rangle + R_0 \langle I_x^2 + I_y^2 \rangle. \tag{57}$$

The term $R_0 \langle I_x^2 + I_y^2 \rangle$ in Eq. (57) is associated with the driving of the resonator by the transverse spin components, while the term $R_h \langle I_z \rangle$ is associated with spin transitions stimulated by the quantum and thermal fluctuations of the resonator.

The secular spin Hamiltonian H_{spin} can affect the polarization process in two ways: (1) By modifying the structure of the spin-spin correlations in the energy eigenstates, and (2) by splitting the degeneracy of energy eigenstates, so that zero-frequency off-diagonal terms in the density matrix are converted to oscillating coherences. Both of these mechanisms affect the polarization process by modifying spin-spin correlations that determine how strongly the transverse spin dipole drives the resonator. With the first mechanism, the spin Hamiltonian modifies these correlations directly, while with the second, it modifies them indirectly by suppressing the development of resonator-induced correlations that would otherwise be present.

For a system of isochronous spins that interact only with the resonator, spin angular momentum is conserved by the interaction Hamiltonian, and the resonator cannot relax the spins to thermal equilibrium. In the limiting case where the resonator temperature is 0 K, for instance, any population which begins outside of the $I = N/2$ manifold cannot relax to the ground state since the spin-resonator interaction cannot transfer the population between angular-momentum manifolds. Rather, each manifold reaches an independent thermal equilibrium with the resonator. This trapping of the spin system away from a thermal distribution is due to the fact that for the ground state of each manifold, the energy transfers associated with transverse spin fluctuations and with the resonator's zero-point fluctuations exactly cancel.

The development of resonator-induced spin-spin correlations in such a system can be visualized using a semiclassical model in which the precessing spins drive a classical resonator that quickly reaches a steady-state response to the torques exerted by the spins. The resonator's field at spin k includes a contribution due to driving by spin j, and the motion of spin j therefore affects the torque acting on spin k. Such indirect torques link each pair of spins and cause the development of spin-spin correlations. The semiclassical model also highlights the difference between radiation damping and resonator-induced polarization since radiation damping is adequately described by the model, while the polarization of a spin 1/2 is not.

In the case where the eigenstates of H_{spin} can be chosen as product states, spontaneous emission by the eigenstates can be interpreted as independent emission by individual spins. Under these conditions, spin-spin correlations that slow the rate of spontaneous emission appear as zero-quantum operators, which develop as a result of resonator-induced couplings between the populations and off-diagonal elements of the density matrix. If the frequencies of these off-diagonal elements are shifted sufficiently far from zero by the chemical-shift Hamiltonian H_{CS}, then the transfers from the populations to these zero-quantum operators are averaged to zero, and the spins relax exponentially to thermal equilibrium with the resonator.

When the spin Hamiltonian includes significant contributions from the homonuclear dipolar coupling H_D, the energy eigenstates involve correlated motions of the spins. In systems containing two or three spins, the symmetry of angular momentum conservation is not fully broken by H_D. The resonator-induced relaxation of two or three spins evolving under this Hamiltonian will in general leave a fraction of the population trapped in states that cannot relax to a lower-energy state. Simulations of cooling in dipole-dipole-coupled systems of four or five spins suggest that such systems contain weakly emitting eigenstates that require time periods $\gg 100/R_0$ to relax to lower-energy states. When a distribution of high-field chemical shifts for H nuclei is added to these simulations, the emission rates of such states tend to increase, enabling transitions to states that can quickly relax to thermal equilibrium.

We conclude by mentioning two additional mechanisms by which the symmetry of angular-momentum conservation could be broken experimentally. First, note that if the coupling constant

$$g \propto \frac{dB_x}{d\theta}$$

varies substantially across the spin sample, the symmetry of the spin-resonator interaction is broken. In Sec. VI A, we showed that the zero emission rate of the state

$$\frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle)$$

is due to the fact that probability amplitudes transferred from $|+-\rangle$ and $|-+\rangle$ to the ground state sum to zero when the spins are in this correlated state. For a slowly emitting spin eigenstate involving several correlated spins, variation in the spin-resonator coupling constants of the correlated spins would in general perturb the symmetry that causes the transferred probability amplitudes to cancel. Variation in the resonator field across the sample would therefore be expected to inhibit trapping, both by introducing a range of Larmor frequencies, which would appear as a chemical-shift Hamiltonian, and by introducing variation in the spin-resonator coupling constants of the correlated spins.

An additional possibility for breaking the symmetry responsible for slow spontaneous emission is to modulate the spin Hamiltonian. If the spin system were temporarily moved out of the large applied field, for instance, the nonsecular part of the dipolar Hamiltonian would be "turned on," and we could expect a spin temperature to be established while the spins are out of resonance with the mechanical oscillator. Moving the spins back into the high field would restore the resonant interaction responsible for enhanced spontaneous emission, but with the spins in a thermal state rather than trapped in a weakly emitting state. Moving the spin-resonator system adiabatically into and out of the high field might thus disrupt any trapping of the spin population in such states.

APPENDIX A: DERIVATION OF THE REDUCED MASTER EQUATION

Equation (15) can be generalized beyond the case where H_1 governs the interactions between a system of spins 1/2 and a resonator whose bandwidth is broad compared to the spectral width of $H_{\rm spin}$. The authors of Ref. [31] derived general formulas for the relaxation superoperator associated with the weak coupling of a small system to a reservoir, and it is straightforward to apply the steps of this derivation to the spin-resonator system, with the damped resonator treated as a thermal reservoir. Using H_1 as the interaction Hamiltonian, we obtain the coarse-grained derivative

$$\begin{aligned}\frac{\Delta\tilde{\rho}}{\Delta t} = -\frac{g^2}{\Delta t}\int_t^{t+\Delta t} dt' \Bigg[&\left(\int_0^\infty d\tau \langle \tilde{a}^\dagger(\tau)\,\tilde{a}(0)\rangle_{\rm th}\tilde{I}_+(t')\tilde{I}_-(t'-\tau)\right)\tilde{\rho}(t) + \left(\int_0^\infty d\tau \langle \tilde{a}(\tau)\,\tilde{a}^\dagger(0)\rangle_{\rm th}\tilde{I}_-(t')\tilde{I}_+(t'-\tau)\right)\tilde{\rho}(t)\\ &\times\tilde{\rho}(t)\left(\int_0^\infty d\tau \langle \tilde{a}^\dagger(0)\,\tilde{a}(\tau)\rangle_{\rm th}\tilde{I}_+(t'-\tau)\tilde{I}_-(t')\right) + \tilde{\rho}(t)\left(\int_0^\infty d\tau \langle \tilde{a}(0)\,\tilde{a}^\dagger(\tau)\rangle_{\rm th}\tilde{I}_-(t'-\tau)\tilde{I}_+(t')\right)\\ &-\left(\int_0^\infty d\tau \langle \tilde{a}(\tau)\,\tilde{a}^\dagger(0)\rangle_{\rm th}\tilde{I}_+(t'-\tau)\tilde{\rho}(t)\,\tilde{I}_-(t')\right) - \left(\int_0^\infty d\tau \langle \tilde{a}^\dagger(\tau)\,\tilde{a}(0)\rangle_{\rm th}\tilde{I}_-(t'-\tau)\tilde{\rho}(t)\,\tilde{I}_+(t')\right)\\ &-\left(\int_0^\infty d\tau \langle \tilde{a}(0)\,\tilde{a}^\dagger(\tau)\rangle_{\rm th}\tilde{I}_+(t')\tilde{\rho}(t)\,\tilde{I}_-(t'-\tau)\right) - \left(\int_0^\infty d\tau \langle \tilde{a}^\dagger(0)\,\tilde{a}(\tau)\rangle_{\rm th}\tilde{I}_-(t')\tilde{\rho}(t)\,\tilde{I}_+(t'-\tau)\right)\Bigg],\end{aligned} \tag{A1}$$

where nonsecular terms have been neglected. The subscript "th" here indicates a thermal expectation value for the resonator. Note that although we have simplified the notation in the main body of the paper by neglecting to distinguish between the interaction-frame operators and laboratory-frame operators, tildes are used in Eq. (A1) and throughout this Appendix to denote interaction-frame operators.

If the evolution associated with $H_{\rm spin}$ is slow enough that it may be neglected in deriving the relaxation superoperator, then the time dependence of the raising and lowering operators is simple: $\tilde{I}_+(t) = e^{i\omega_0 t}I_+$ and $\tilde{I}_-(t) = e^{-i\omega_0 t}I_-$. In this case the integrals over τ in Eq. (A1) can be simplified significantly; for example,

$$\begin{aligned}&\left(\int_0^\infty d\tau \langle \tilde{a}^\dagger(\tau)\,\tilde{a}(0)\rangle_{\rm th}\tilde{I}_+(t')\tilde{I}_-(t'-\tau)\right)\\ &= \left(\int_0^\infty d\tau \langle \tilde{a}^\dagger(\tau)\,\tilde{a}(0)\rangle_{\rm th}e^{i\omega_0\tau}\right)I_+I_-\\ &= \tau_h n_{\rm th} I_+I_-,\end{aligned} \tag{A2}$$

where the correlation function

$$\langle\tilde{a}^\dagger(\tau)\tilde{a}(0)\rangle_{\rm th} = n_{\rm th}\,e^{i\omega_h t}e^{-t/\tau_h}$$

has been evaluated using the master equation for a damped harmonic oscillator [40]. (The authors of Ref. [51] discussed the approximations involved in using a master equation to calculate correlation functions and also provided a detailed explanation of how such calculations are performed.) Evaluating the integrals in Eq. (A1) yields the spin-relaxation superoperator of Eq. (16), without the restriction $I = 1/2$.

In the case where an off-resonant mechanical mode is inducing spin relaxation, a reduced master equation can easily be derived from Eq. (A1). Defining

$$\Delta\omega = \omega_h - |\omega_0|$$

and evaluating the correlation functions in Eq. (A1), we find that the superoperator Λ of Eq. (16) is replaced by $\Lambda' + \Lambda''$, where

$$\begin{aligned}\Lambda'\rho = {}& R_0'(n_{\rm th}+1)\left(I_+\rho I_- - \tfrac{1}{2}[I_-I_+,\rho]_+\right)\\ &+ R_0' n_{\rm th}\left(I_-\rho I_+ - \tfrac{1}{2}[I_+I_-,\rho]_+\right)\end{aligned} \tag{A3}$$

and

$$\Lambda''\rho = \tfrac{1}{2}R_0''\{(n_{\rm th}+1)[I_-I_+,\rho] - n_{\rm th}[I_+I_-,\rho]\}. \tag{A4}$$

In Eqs. (A3) and (A4), R_0' and R_0'' are the respective real and imaginary components of a complex Lorentzian:

$$\begin{aligned}R_0' &= 2g^2\frac{\tau_h}{1+(\Delta\omega\,\tau_h)^2},\\ R_0'' &= 2g^2\frac{i\,\Delta\omega\,\tau_h^2}{1+(\Delta\omega\,\tau_h)^2}.\end{aligned}$$

Note that R_0'' is associated with frequency shifts of the spin system. If these shifts are neglected, then the superoperator associated with an off-resonant mechanical mode can be obtained by replacing R_0 in Eq. (16) with R_0' (i.e., by scaling down R_0 to take account of the spectral density of the mechanical fluctuations at the Larmor frequency).

Equation (A1) can also be used to characterize the way in which the polarization process is affected if the spectral width of $H_{\rm spin}$ is comparable to or larger than the resonator bandwidth. The approximation of a narrow bandwidth for $H_{\rm spin}$ is equivalent to assuming that $\tilde{I}_+(t')\tilde{I}_-(t'-\tau)$ is resonant with $\langle\tilde{a}^\dagger(\tau)\tilde{a}(0)\rangle_{\rm th}$ in Eq. (A2), and a similar statement can be made for each of the correlations functions in Eq. (A1). Increasing the bandwidth of $H_{\rm spin}$ beyond that of the resonator will move some single-quantum transitions out of resonance, diminishing or eliminating the enhancement to spontaneous emission for these transitions.

If the correction H_2 of Eq. (13) is added to the interaction Hamiltonian, the coarse-grained derivative of Eq. (A1) is

modified by the addition of the following secular terms:

$$-\frac{w^2}{\Delta t}\int_t^{t+\Delta t} dt' \times \Big[I_z^2\,\tilde{\rho}\,(t)\int_0^\infty d\tau\,\langle \tilde{f}\,(\tau)\,\tilde{f}\,(0)\rangle_{\rm th} + \tilde{\rho}\,(t)\,I_z^2\int_0^\infty d\tau\,\langle \tilde{f}\,(0)\,\tilde{f}\,(\tau)\rangle_{\rm th} - I_z\,\tilde{\rho}\,(t)\,I_z\int_0^\infty d\tau\,\langle \tilde{f}\,(\tau)\,\tilde{f}\,(0)+\tilde{f}\,(0)\,\tilde{f}\,(\tau)\rangle_{\rm th}\Big],$$

where

$$\tilde{f} = \tilde{a}^\dagger\tilde{a} - n_{\rm th}.$$

From the master equation for a damped harmonic oscillator [40], we obtain

$$\langle \tilde{f}\,(\tau)\,\tilde{f}\,(0)\rangle_{\rm th} = \langle \tilde{f}\,(0)\,\tilde{f}\,(\tau)\rangle_{\rm th} = e^{-2t/\tau_h}\langle \tilde{f}^2\rangle_{\rm th}.$$

The term

$$\langle \tilde{f}^2\rangle_{\rm th} = \langle a^\dagger a a^\dagger a\rangle_{\rm th} - n_{\rm th}^2$$

can be evaluated by using the master equation to obtain a relaxation equation for $\langle a^\dagger a a^\dagger a\rangle$ and then finding the steady-state solution, which corresponds to thermal equilibrium. We find that the inclusion of H_2 in the interaction Hamiltonian introduces an additional term Λ_2 into the spin relaxation superoperator, given by

$$\Lambda_2\rho = C_2\left(I_z\rho I_z - \tfrac{1}{2}\left[I_z^2,\rho\right]_+\right), \tag{A5}$$

$$C_2 = w^2\tau_h n_{\rm th}(n_{\rm th}+1). \tag{A6}$$

A comparison of Eqs. (A5) and (A6) with Eqs. (16) and (17) suggests that the ratio $(n_{\rm th}+1)w^2/g^2$ can be used to roughly characterize the relative magnitude of the contributions to the spin relaxation associated with H_2 and H_1. In Sec. III C 1, this ratio is shown to be negligible for the example resonator found in Ref. [21] over a wide range of temperatures.

APPENDIX B: DERIVATION OF THE SEMICLASSICAL EQUATION FOR LONGITUDINAL RELAXATION

In deriving a semiclassical equation for longitudinal relaxation, we begin by showing that the quantum mechanical equation of motion can be obtained by expressing $\langle I_z(t)\rangle$ as an iterated integral, where each integrand is the expectation value of an operator that acts on the spin-resonator system. We then show that a similar iterated integral can be obtained for the semiclassical system.

To motivate the approach, we recall that a master equation of the form

$$\frac{d}{dt}\sigma\,(t) = L\sigma\,(t)$$

can be transformed into an integral equation:

$$\sigma\,(t) = \sigma\,(0) + \int_0^t dt_1\,L\sigma\,(t_1)\,.$$

Replacing the density matrix $\sigma\,(t_1)$ appearing in the integrand by an integral equation for $\sigma\,(t_1)$ yields

$$\sigma\,(t) = \sigma\,(0) + \int_0^t dt_1\,L\sigma\,(0) + \int_0^t dt_1\int_0^{t_1} dt_2\,L^2\sigma(t_2)\,.$$

Repeating the process of substituting an integral equation for the time-dependent integrand yields a series expansion in which successive terms depend on higher powers of the superoperator L.

An analogous process can be used to obtain a series expansion of the coarse-grained derivative $\Delta\langle I_z\rangle/\Delta t$, where Δt is short on the time scale of the spin relaxation. If $H_{\rm spin} = 0$, the evolution of the spin-resonator density matrix σ is governed by the master equation [28,29]

$$\frac{d\sigma}{dt} = -i[H_1,\sigma] + \Lambda_{\rm osc}\sigma, \tag{B1}$$

where $\Lambda_{\rm osc}$ is the relaxation superoperator for a damped harmonic oscillator [40]. Equation (B1) is used to find the instantaneous derivative $d\langle I_z\rangle/dt$, and this derivative is transformed into an integral equation for $\langle I_z\rangle$:

$$\langle I_z\rangle\,(t) = \langle I_z\rangle\,(0) + \int_0^t dt_1\,(-ig)\langle I_+a^\dagger - I_-a\rangle(t_1). \tag{B2}$$

The time-dependent quantities appearing in the integrand are themselves replaced by integral equations derived from the full master equation, and the process is repeated to yield a series expansion for $\langle I_z\rangle(t)$ in powers of the coupling constant g:

$$\langle I_z\rangle(t) = \langle I_z\rangle(0) - ig\langle I_+a^\dagger - I_-a\rangle\,(0)\int_0^{\Delta t} dt_1\,e^{-t_1/\tau_h} - 4g^2\langle I_z a^\dagger a\rangle\,(0)\int_0^{\Delta t} dt_1\,e^{-t_1/\tau_h}\int_0^{t_1} dt_2\,e^{-t_2/\tau_h} - 4g^2 n_{\rm th}\langle I_z\rangle\,(0) \times \int_0^{\Delta t} dt_1\,e^{-t_1/\tau_h}\int_0^{t_1} dt_2\,e^{t_2/\tau_h}(1-e^{-2t_2/\tau_h}) + 2g^2\langle I_-I_+\rangle\,(0)\int_0^{\Delta t} dt_1\,e^{-t_1/\tau_h}\int_0^{t_1} dt_2\,e^{t_2/\tau_h} + O(g^3). \tag{B3}$$

This coarse-grained derivative is correct to second order in the coupling constant g, regardless of the relative sizes of τ_h and Δt. In the case where

$$\tau_h \ll \Delta t, \tag{B4}$$

negligible error is introduced by considering the resonator and spins to be uncorrelated at time $t = 0$ since correlations present at the beginning of the time step make a contribution to the motion only during an initial time period of order τ_h, which is a small fraction of the integrated time period Δt [31]. Indeed, we may consider the resonator to be in a thermal state at time $t = 0$ since Eq. (B4) implies that the spin-resonator interaction only weakly perturbs the resonator from its thermal state. This approximation yields

$$\langle I_+a^\dagger - I_-a\rangle\,(0) = 0,$$
$$\langle I_z a^\dagger a\rangle\,(0) = n_{\rm th}\langle I_z\rangle.$$

Evaluating the integrals of Eq. (B3) and using Eq. (B4) to simplify the resulting expression gives

$$\frac{\Delta\langle I_z\rangle}{\Delta t} = -2R_0 n_{\rm th}\langle I_z\rangle + R_0\langle I_- I_+\rangle, \tag{B5}$$

where

$$\Delta\langle I_z\rangle = \langle I_z\rangle(t) - \langle I_z\rangle(0).$$

Note that Eq. (B5) is equivalent to Eq. (18), the equation of motion for $\langle I_z\rangle$ obtained directly from the reduced master equation.

The steps used to obtain Eq. (B5) from the iterated integral equation (B3) do not depend on the quantum mechanical nature of the system, and a semiclassical equation similar to Eq. (B5) can be obtained by first deriving a semiclassical iterated equation similar to Eq. (B3). This can be done by defining the semiclassical variables analogous to the operators appearing in Eq. (B3), and then using the rules of calculus, in combination with some physical reasoning, to obtain the iterated integral equation.

To simplify notation, we use $\mathbf{I}$ rather than $\mathcal{I}$ to represent the semiclassical spin vector. The motion of $\mathbf{I}$ is governed by Eq. (29),

$$\frac{d}{dt}\mathbf{I} = \gamma\mathbf{I}\times\mathbf{B}, \tag{B6}$$

while the evolution of the resonator's torsional coordinate θ and angular momentum p_θ are governed by the equations

$$\frac{d}{dt}\theta = \frac{1}{I_h}p_\theta - \frac{1}{\tau_h}\theta, \tag{B7a}$$

$$\frac{d}{dt}p_\theta = -I_h\omega_h^2\theta - \frac{1}{\tau_h}p_\theta + f(t), \tag{B7b}$$

where $f(t)$ is the driving torque. It follows from Eq. (30) that

$$f(t) = \frac{dB_x}{d\theta}\gamma\hbar I_x(t) + N(t),$$

where $N(t)$ is the thermal torque. Semiclassical analogs of the raising and lowering operators for the spins and the resonator are defined in the same way as the quantum operators,

$$a = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{I_h\omega_h}{\hbar}}\theta + i\sqrt{\frac{1}{I_h\omega_h\hbar}}p_\theta\right),$$

$$a^\dagger = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{I_h\omega_h}{\hbar}}\theta - i\sqrt{\frac{1}{I_h\omega_h\hbar}}p_\theta\right),$$

$$I_+ = I_x + iI_y,$$

$$I_- = I_x - iI_y,$$

and we move to a "semiclassical interaction frame" by multiplying these variables by exponentials which cancel the time dependence associated with the fast, unperturbed motion of the uncoupled system:

$$\begin{aligned}\tilde{a} &= e^{i\omega_h t}a,\\ \tilde{a}^\dagger &= e^{-i\omega_h t}a^\dagger,\\ \tilde{I}_+ &= e^{-i\omega_0 t}I_+,\\ \tilde{I}_- &= e^{i\omega_0 t}I_-.\end{aligned} \tag{B8}$$

The right side of Eq. (B6) is then expressed in terms of these interaction-frame variables, and the quickly oscillating terms are discarded, as in the rotating-wave approximation. A simplification of the resulting equations yields

$$\frac{d}{dt}I_z = -ig(\tilde{I}_+\tilde{a}^\dagger - \tilde{I}_-\tilde{a}) \tag{B9}$$

and

$$\frac{d}{dt}\tilde{I}_+ = -2igI_z\tilde{a}. \tag{B10}$$

The derivative of $\tilde{a}$ is found by differentiating Eq. (B8), substituting Eqs. (B7a) and (B7b) into the derivative, writing the resulting equation in the interaction frame, and then making the rotating-wave approximation:

$$\frac{d}{dt}\tilde{a} = -\frac{1}{\tau_h}\tilde{a} - ig\tilde{I}_+ + \frac{i}{\sqrt{2I_h\omega_h\hbar}}e^{i\omega_h t}N. \tag{B11}$$

The product rule of elementary calculus, in combination with Eqs. (B9), (B10), and (B11), is used to obtain an integral equation similar to Eq. (B2), as well as integral equations for $\langle I_+a^\dagger - I_-a\rangle$, $\langle I_z a^\dagger a\rangle$, and $\langle I_- I_+\rangle$. These yield an iterated integral similar to Eq. (B3), where $n_{\rm th}$ is replaced by $\langle E_h\rangle/\hbar\omega_h$. It follows that the semiclassical coarse-grained derivative is

$$\frac{\Delta\langle I_z\rangle}{\Delta t} = -2R_0\frac{\langle E_h\rangle}{\hbar\omega_h}\langle I_z\rangle + R_0\langle I_- I_+\rangle. \tag{B12}$$

The integral equations used to derive Eq. (B12) are averages over a statistical ensemble, and physical reasoning is needed to evaluate the statistical averages of certain variables. The remainder of this Appendix outlines the necessary reasoning. First, we note that the correlations between spin variables and the thermal torque on the resonator can be neglected. The thermal motion of the resonator is a sum of decaying responses to many uncorrelated impulses, with each impulse response contributing only weakly to the motion. The correlations between the spin motion and a given thermal impulse $N(t)$ depends on the spins' response during the impulse to the small fraction of the resonator motion which results from that impulse, and can thus be neglected. Greater care is needed in evaluating the laboratory-frame correlation $\langle I_z p_\theta N\rangle$, which contributes to the time derivative of $\langle I_z a^\dagger a\rangle$. We note that the resonator evolves under the influence of two types of torques: the torques exerted by the spins and the thermal torque exerted by the reservoir. We may thus write p_θ as

$$p_\theta = p_\theta^S + p_\theta^R,$$

where p_θ^S and p_θ^R give the resonator's response to the respective torques associated with the spins and the reservoir. Under the approximation that the spin variables and the thermal torque N are uncorrelated, both I and p_θ^S are statistically independent of the thermal torque N, and we can write

$$\begin{aligned}\langle I_z p_\theta N\rangle &= \left\langle I_z p_\theta^S\right\rangle\langle N\rangle + \left\langle I_z p_\theta^R N\right\rangle\\ &= \left\langle I_z p_\theta^R N\right\rangle.\end{aligned}$$

The neglect of correlations between I_z and $p_\theta^R N$ is justified, once again because such correlations depend on the spins' response during an impulse to the small fraction of the

resonator motion caused by that impulse. It follows that

$$\langle I_z p_\theta N\rangle \approx \langle I_z\rangle\langle p_\theta^R N\rangle.$$

In obtaining an explicit expression for the thermal average $\langle p_\theta^R N\rangle$, we consider a resonator which interacts only with a reservoir and is in thermal equilibrium with it, simplifying the notation by dropping the superscript "R" from p_θ. We calculate the derivative dE_h/dt, where

$$E_h = \frac{1}{2I_h}p_\theta^2 + \frac{I_h\omega_h^2}{2}\theta^2$$

is the resonator energy, substitute Eqs. (B7a) and (B7b) into the resulting derivative, and set dE_h/dt to zero since the resonator is in thermal equilibrium. In this way, we we find that $\langle p_\theta N\rangle = (2I_h/\tau_h)\langle E_h\rangle$, which gives

$$\langle I_z p_\theta N\rangle = \frac{2I_h}{\tau_h}\langle E_h\rangle\langle I_z\rangle.$$

APPENDIX C: TIME SCALE FOR THE DEVELOPMENT OF RESONATOR-INDUCED CORRELATIONS

An analysis based on Eqs. (18) and (36) supports the semiclassical estimate (41) of the time needed for the development of resonator-induced spin-spin correlations when the initial spin state is disordered. From Eq. (18), the relaxation of $\langle I_z\rangle$ at 0 K is governed by

$$\frac{d}{dt}\langle I_z\rangle = R_0\big(\langle I_x^2 + I_y^2\rangle - \langle I_z\rangle\big). \tag{C1}$$

Setting $d\langle I_z\rangle/dt = 0$ for the trapped state and recalling from Eq. (36) that $P_{\rm trap} \approx \sqrt{2/N}$ for a system of $N \gg 1$ spins 1/2 that are initially disordered, we find that the steady-state values of $\langle I_z\rangle$ and $\langle I_x^2 + I_y^2\rangle$ in the trapped state are

$$\langle I_z\rangle_{\rm trap} \approx \langle I_x^2 + I_y^2\rangle_{\rm trap} \approx \sqrt{N/2}.$$

Let us accept for the moment the claim that $\langle I_x^2 + I_y^2\rangle$ decreases monotonically from $N/2$ to $\sqrt{N/2}$ as spin-spin correlations develop. Then Eq. (C1) implies that $\langle I_z\rangle$ grows monotonically from its initial value of 0 toward $\sqrt{N/2}$, with the growth slowing as the difference between $\langle I_z\rangle$ and $\langle I_x^2 + I_y^2\rangle$ diminishes. Since the growth of $\langle I_z\rangle$ is continually slowing, we can obtain a lower bound on the time needed for relaxation from 0 to $\langle I_z\rangle_{\rm trap}$ by calculating the time that would be required if the growth of $\langle I_z\rangle$ continued at its initial rate, rather than slowing. The initial value of the derivative dI_z/dt is $R_0N/2$, and so this bound is given by the ratio

$$\frac{\langle I_z\rangle_{\rm trap}}{R_0N/2} = \frac{1}{R_0\sqrt{N/2}}. \tag{C2}$$

This bound can serve as a estimate of the time needed for the nonnegligible relaxation of $\langle I_z\rangle$ toward its trapped value.

Rewriting Eq. (C1) in the form

$$\langle I_x^2 + I_y^2\rangle = \langle I_z\rangle + \frac{1}{R_0}\frac{d}{dt}\langle I_z\rangle$$

shows that the times scales for the relaxation of $\langle I_z\rangle$ and $\langle I_x^2 + I_y^2\rangle$ to their steady-state values are roughly similar: as $\langle I_z\rangle \to \langle I_z\rangle_{\rm trap}$, it must also be true that $d\langle I_z\rangle/dt \to 0$ and $\langle I_x^2 + I_y^2\rangle \to \langle I_x^2 + I_y^2\rangle_{\rm trap}$. The characteristic evolution time for $\langle I_z\rangle$ obtained in Eq. (C2),

$$T_{\rm trap} = (R_0\sqrt{N/2})^{-1}, \tag{C3}$$

can thus also serve as an estimate of the time needed for the development of the resonator-induced correlations that suppress spontaneous emission.

In considering the claim that $\langle I_x^2 + I_y^2\rangle$ decreases monotonically if the initial state is completely disordered, we first note that resonator-induced relaxation in such a system is completely characterized by the population transfers occurring within each angular momentum manifold. It is therefore sufficient to consider the evolution of $\langle I_x^2 + I_y^2\rangle$ in a single manifold of states $|I,M\rangle$, where I is the total angular momentum, and M is the z component. The states $|I,M\rangle$ are eigenstates of the operator $I_x^2 + I_y^2$:

$$\big(I_x^2 + I_y^2\big)|I,M\rangle = [I(I+1) - M^2]|I,M\rangle.$$

For $\gamma > 0$ (as assumed in this paper), the ground state of a given manifold has $M = I$, and spontaneous emission moves the population toward this state. It is clear that once the bulk of the population in a given manifold has relaxed to states with positive M, continued spontaneous emission will decrease $\langle I_x^2 + I_y^2\rangle$ since the emission from a state with positive M increases the value of $|M|$ by 1 and thereby decreases the value of $[I(I+1) - M^2]$. To investigate the evolution during the initial part of the relaxation, in which some population is relaxing from states with higher M^2 to states with lower M^2, we simulated resonator-induced cooling within single angular-momentum manifolds, with all states $|I,M\rangle$ initially having equal population. For several values of I between $I = 2$ and $I = 100$, we verified that $\langle I_x^2 + I_y^2\rangle$ decreases monotonically. Simulations of the relaxation of a 36-spin system and a 144-spin system also showed a monotonic decay of $\langle I_x^2 + I_y^2\rangle$.

APPENDIX D: LONGITUDINAL RELAXATION DUE TO COUPLING BETWEEN PRODUCT-STATE POPULATIONS

Section VI A shows that if product states can be chosen as eigenstates of the spin Hamiltonian for a system of two spins 1/2, and if resonator-induced transfers between product-state populations and off-diagonal terms of the density matrix are efficiently averaged to zero by $H_{\rm CS}$, then $\langle I_{1z}\rangle$ and $\langle I_{2z}\rangle$ each relax exponentially to their thermal value with rate constant R_h, regardless of the initial state. In generalizing this result to a system of N spins, we first note that the interaction Hamiltonian H_1 couples product-state populations ρ_{aa} and ρ_{bb} only if states $|a\rangle$, $|b\rangle$ differ by exactly one spin flip. Without loss of generality, suppose that $|a\rangle$ is the lower-energy state. Then the respective rate constants

$$\mathcal{R}_{bbaa} = R_h n_{\rm th}, \tag{D1a}$$

$$\mathcal{R}_{aabb} = R_0(n_{\rm th} + 1) \tag{D1b}$$

for population transfer from $|a\rangle \to |b\rangle$ and from $|b\rangle \to |a\rangle$ have the same values as they would if $|a\rangle$ and $|b\rangle$ were states $|+\rangle$ and $|-\rangle$, respectively, of a single spin interacting with the resonator.

Assume that transfers between populations and off-diagonal terms of the density matrix are suppressed. The net

change in the populations that occurs during a short time step Δt by can be calculated by summing all direct transfers between populations, and these transfers may be considered to occur in any order we choose. We initially focus our attention on an arbitrary spin k, and we take Z_k to be the set of rate constants $\mathcal{R}_{ccdd}$ that govern the population transfer between states differing by a flip of spin k. We will show below that if all transfers associated with Z_k are summed, and if these are the only transfers that are summed, then $\langle I_{kz}\rangle$ relaxes exactly as if spin k were an isolated spin being polarized by the resonator, while $\langle I_{jz}\rangle$ is unchanged, for $j \neq k$. By sequentially summing the population transfers associated with $Z_1, Z_2, \ldots$, we find that the longitudinal components $\langle I_{1z}\rangle, \langle I_{2z}\rangle, \ldots$, each relax toward their thermal values during Δt just as if each spin were interacting independently with the resonator. It follows that $\langle I_z\rangle$ relaxes to its thermal value regardless of the initial spin state.

Group the product states of the spin system into pairs, with the states of each pair differing by a flip of spin k. Let $|u+\rangle$, $|u-\rangle$ denote the respective states of pair u for which spin k is oriented parallel and antiparallel to B_z. Define

$$\rho_+ = \sum_u \rho_{u+},$$
$$\rho_- = \sum_u \rho_{u-},$$

where ρ_{u+}, ρ_{u-} denote the respective populations of the states $|u+\rangle$, $|u-\rangle$. It follows from Eqs. (D1a) and (D1b) that the population transfers associated with Z_k cause ρ_{u+} and ρ_{u-} to evolve during the time step Δt exactly as if they were the populations of an isolated spin interacting with the resonator:

$$\Delta\rho_{u+} = [-R_0 n_{\rm th}\,\rho_{u+} + R_0(n_{\rm th}+1)\rho_{u-}]\Delta t,$$
$$\Delta\rho_{u-} = [-R_0(n_{\rm th}+1)\rho_{u-} + R_0 n_{\rm th}\,\rho_{u+}]\Delta t.$$

We find that

$$\begin{aligned}\Delta\rho_+ &= \sum_u \Delta\rho_{u+} \\ &= \sum_u [-R_0 n_{\rm th}\,\rho_{u+} + (R_0 n_{\rm th}+1)\rho_{u-}]\Delta t, \\ &= [-R_0 n_{\rm th}\,\rho_+ + (R_0 n_{\rm th}+1)\rho_-]\Delta t, \end{aligned} \tag{D2}$$

and similarly

$$\Delta\rho_- = [-R_0(n_{\rm th}+1)\rho_- + R_0 n_{\rm th}\,\rho_+]\Delta t. \tag{D3}$$

Since $\langle I_{kz}\rangle$ is given by

$$\langle I_{z,k}\rangle = \tfrac{1}{2}\rho_+ - \tfrac{1}{2}\rho_-,$$

Eqs. (D2) and (D3) imply that the transitions associated with Z_k cause $\langle I_{kz}\rangle$ to relax as if spin k were interacting independently with the resonator.

Note that for each pair u, the sum

$$\rho_u \equiv \rho_{u+} + \rho_{u-}$$

does not change during these transitions, and that for $j \neq k$, we have

$$\langle I_{jz}\rangle = \sum_u \lambda_{jz}\,\rho_u,$$

where λ_{jz} is the eigenvalue of I_{jz} for the two states in pair u. Since ρ_u does not change during these transitions, $\langle I_{jz}\rangle$ is also unchanged. This establishes our claim that direct coupling between product-state populations, in the absence of any coupling between populations and off-diagonal terms, causes $\langle I_z\rangle$ to relax exponentially to its thermal value with rate constant R_h.

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